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Integration of energy harvesting and electrochemical storage devices

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Abstract

Multifunctional energy devices with various energy forms in different operation modes are emerging to meet the ever-increasing demand for future advanced smart electronics. Currently, substantial efforts are being devoted to designing new combination systems or integrated devices with different functions together. In this review, we summarize the recent progress made in developing integrated/joint multifunctional devices, with a focus on electrochromic batteries/supercapacitors and solar cells + batteries/supercapacitors. The concepts and design strategies are highlighted with discussion on their merit/demerits. Our opinions on future research to smart multifunctional energy-associated devices are provided at the end.

1. Introduction to integrated multifunctional electrodes/devices

A smart and full manipulation of energy harvest, conversion and storage plays a vital role in reducing the energy consumption and environmental load.^[1, 2] Recent technological trends toward high-performance smart electronics have stimulated the demand for multifunctional devices or integrated systems,^[3, 4] which are essential for the future development of implantable biosensors, smart windows, foldable displays and wearable electronics.^[5-9] For instance, it would be particularly attractive to integrate electrochromism and energy harvesting as well as storage functions into smart windows.^[10] Through electrochromic tunability, smart windows on buildings are able to phase out the curtains and reduce the energy consumption dramatically by decreasing the cooling or heating load.^[11-17] Meanwhile, the smart windows can harvest and store the solar energy at the daytime and power the building in the night.^[18] Such a smart combination not only provides multifunctional systems, but also saves materials and footprint in modern smart house. Another example is the wireless operation devices such as unmanned aerial vehicles and implantable biosensors, which are required to be placed in remote areas or hazardous conditions. They are required to be self-charged/powered by converting other energy forms from natural sources (heat, solar, wind etc.) or human body (piezoelectricity, tribology, and so on) into their usable power sources.^[19-23] Moreover, the harvested energy must be stored at the same time to make it possible to power themselves for a long time without any maintenance.^[24-26] In this context,

multifunctional devices/materials with multi-roles are the most promising for the future development of self-powered smart devices.

Electrochemical energy storage (EES) system is one of the most important parts in integrated smart devices.^[2, 27-35] The current dominant EES systems include lithium ion batteries (LIBs) and supercapacitors.^[36-39] The former generally possess high energy density but with relatively low power density,^[27, 40-43] whereas the latter have the opposite advantage and are typically used for high power applications due to the different working mechanisms.^[44-48] However, the common EES devices require external power source and intensive maintenance. But this is not feasible in deserts or other uninhabited areas. In view of this situation, it is a critical task to develop self-powered smart devices combined with energy harvest/conversion and storage units.^[49]

Currently, continuous efforts have been devoted to fabricating new integrated/joint systems to combine energy harvesting/conversion components with conventional single-functional devices. The harvesting component can capture the energy from surroundings and convert into usable energy to power electrical devices.^[30, 50, 51] For example, Wang and coworkers fabricated a series of self-powered devices driven by piezoelectric nanogenerators and triboelectric nanogenerators, including self-powered electrochromic devices, water splitting systems and sensors.^[52-56] Such nanogenerators convert the small magnitude of mechanical energy in our living environment into electricity. In addition, silicon based photovoltaic cells, perovskite and dye-sensitized solar cells have also been integrated into electrochromic devices to achieve self-powered operation and maximize energy savings/utilization.^[57, 58]

Along with the above efforts, equal efforts are also paid to miniaturized design such as nano-sized and fiber-shaped energy conversion/storage devices.^[59, 60] **Though planar structured devices have the advantage of simple process and cost effectiveness, they cannot be easily integrated with wearable equipment.** Hence, researchers are developing new materials with attractive properties of being flexible and stretchable, transparent, or responsive and self-healing to meet the increasing demand in the future advanced electronics.^[61-64] For example, Peng and co-workers reported the wearable fiber-shaped multifunctional device with superior flexibility and good energy storage performance.^[62-64]

In this review, we will focus on integrated devices that are related to electrochemical energy. We will review the recent progress made in developing high-performance integrated or joint electrochemical multifunctional systems such as electrochromic batteries/supercapacitors and solar cells-batteries/supercapacitors. Typical examples from recent literature will be presented and their combinational properties will be discussed.

Furthermore, we will address the different design strategies for efficient integrated energy harvesting/storage and their problems/limitations as well as challenges. At the end, we will give an overall summary and our perspective to the future trend in the development of smart multifunctional energy devices.

2. Different types of integration for multi-functionality

There are different expression ways for the multi-functionality associated with electrochemical energy. (1) One is joint combination. In this configuration, different components/devices are connected with each other to form a new multifunctional system. This combination, in general, has two ways: integrated device combination and discontinuous connection. In the former configuration, all functional components are physically connected with each other without external wires, and are fabricated on one chip or a framework.^[18] The integrated configuration is much more challenging and needs sophisticated fabrication of both active materials and device. For the latter (discontinuous connection), they are usually physically separated from each other. For example, the electricity produced by solar cells on the ground may be stored by the batteries/supercapacitors buried underground. (2) The second way is one unit with multiple purposes. In this configuration, one component or active material possesses multiple functions. For example, not only can it be the energy conversion/storage material, but also show other functions such as electrochromics.^[18] This multifunctional device has a relatively simple configuration, but the choice of materials is very limited. To date, several multiple combinations are demonstrated including light energy and electrochemical energy, tribological energy combined with electrochemical energy, and electrochromics plus electrochemical energy. They will be discussed in detail in the following sections.

2.1 Combination of solar and electrochemical energy

Energy harvest/conversion and storage are two critical technologies in an integrated energy system. To date, the dominant energy harvesting techniques include solar energy, mechanical energy and thermal energy. Among them, solar energy is the most sustainable and abundant.^[65] Therefore, most efforts have been made to integrate solar energy harvesting component with energy storage devices to construct sustainable self-powered devices, which have combined properties of electricity generation and storage at the same time. The electric energy generated from solar cells can directly power the device, and meanwhile, the extra

electricity can be stored in the joint electrochemical energy storage components (batteries or supercapacitors).

Solar energy is considered as the most promising clean energy source for the future because it represents an unlimited source of energy and sustainable electricity without toxic pollution or global warming emissions.^[66, 67] Solar cells including silicon solar cells, polymer solar cells (PSCs), perovskite solar cells and dye-sensitized solar cells (DSSCs) have been extensively studied and able to be commercialized.^[58, 68-70] However, the sunlight intensity reaching the earth's surface depends on the time, weather patterns and districts, thus the energy output of the solar cells will fluctuate with intermittency and instability. Accordingly, in some cases, it cannot be directly used as the only power source for electronic devices.^[71, 72] An effective solution is to combine solar cells with energy storage devices to store the generated electricity for later use. The integrated device is also recognized as photovoltaically self-charging cell, which has attracted great scientific and technological attention due to the increasing demand in the electronic industry.^[73-75] The connection mode between the energy storage and energy conversion system can be classified into three main categories (as shown in **Figure 1**): (1) Mode I, the energy conversion and storage units are connected via an external circuit; (2) Mode II, the energy conversion and storage units are connected via an integrated platform; and (3) Mode III, the energy conversion and storage units are integrated into one single unit/chip. In the first two modes, the energy conversion and storage processes are independent, in other words, the solar energy is converted into electricity and then transport to supercapacitors or LIBs for storage. While for the third mode, these two processes are integrated into one step in which the energy is directly converted and simultaneously stored as electrochemical energy without any intermediate processes.^[76] Up to now, mode I is the most common way for the current technologies, and it can be applicable to all types of energy conversion and storage technologies. However, an external circuit is required for mode I and therefore energy loss from electrical resistance is inevitable. Discontinuous solar cell-EES devices have been widely investigated.^[30, 77-90] Unfortunately, such integration modes cause energy loss due to resistance in connections and are not compatible with roll-to-roll printing and other flexible design. Additionally, the disadvantages of LIBs (low power density) and supercapacitors (low energy density) further limit the charge/discharge capability and energy storage efficiency of these integrated PV-battery systems. On the other hand, these traditional systems are cumbersome, rigid, large, and hindering their applications in daily use. Thus, developing high performance system with simple structure, light-weight, flexibility and portability becomes important. Modes II and III are two more sophisticated ways, and may

apply only to certain specific energy conversion technologies due to their delicate fabrication. In addition, their stored energy volume would be restricted by their size because of their unique working principle.

Figure 1. Three types of combination modes between energy conversion and storage devices. Mode I: integration via extra connections; Mode II: integration via a platform, and Mode III: integration into one single unit.

2.1.1 Solar cells - batteries/supercapacitors

2.1.1.1 Dye-sensitized solar cells-batteries/supercapacitors

Dye-sensitized solar cell (DSSC) has the most effective ability to convert solar energy into electricity and have tremendous advantages such as lightweight, low cost and high conversion efficiency ($\eta_{\text{conversion}}$, refers to the ratio of the output maximum power by the solar cell to the input power, Eqn. 1), which are considered to be the next-generation photovoltaic cells for commercial applications.

$$\eta_{\text{conversion}} = \frac{FF \times V_{oc} \times J_{sc}}{P_{in}} \quad (1)$$

where FF , V_{oc} , J_{sc} , and P_{in} correspond to fill factor, open-circuit voltage, short-circuit current density, and incident light power density, respectively.^[91, 92] A typical dye-sensitized solar cells is composed of a working electrode, a counter electrode and an electrolyte containing a redox mediator (usually I^-/I_3^-).^[93] The counter electrode is opaque, so a dye-sensitized solar cell is usually illuminated from the working electrode, thus making it possible to share the counter electrode with the LIB or supercapacitor part, as well as a synergy in structure through the use of a common electrolyte.^[80] In this regards, the design of shared electrode plays a key role in achieving high performance from the integrated energy device.

The traditional configuration usually connects two independent systems by external electrical interconnections (Mode I). Although this combination is simple and low cost, however, it consumes extra resistance loss and needs more space due to the external connections. Therefore, more compact and efficient combination types are more preferable such as Modes II and III. Recently, Yang et al.^[88] reported free-standing and aligned carbon nanotubes (CNTs) film by a simple chemical vapor deposition method and applied as the sharing electrode in a combined energy system as shown in **Figure 2a-c**.^[88] When the working electrode of a DSSC part was connected to the other electrode of the supercapacitor part, the voltage of the integrated device was increased rapidly under illumination, indicating that the charging process was effective and high-efficiency. The voltage was maintained at 0.72 V, a little lower than the open-circuit photo-voltage of the DSSC unit resulting from the voltage loss in the external circuit. After finishing the charging process, the stored electrical energy could be used when the supercapacitor part was connected to the external load. The supercapacitor could be charged again by the DSSC. For this combination, it is of great importance to enhance the capacitance of supercapacitor to improve the storage capability of the integrated device. Given this consideration, high-performance capacitive materials are highly desirable. Metal oxides/hydroxides and conducting polymers have been extensively investigated. For instance, by introduction of pseudocapacitive polyaniline into aligned CNT sheet, the output power of the integrated energy device was greatly improved. Xu et al. adopted hydrogenated bi-polar TiO₂ films for both DSSC and supercapacitor (**Figure 2d-e**).^[30] A sandwich structure was designed in this configuration and only the TiO₂ nanotube arrays at the supercapacitor side were treated by selective hydrogen plasma. Noticeably, enhanced capacitive performance has been achieved in the above system. Correspondingly, the whole performance was reinforcement with an overall conversion and storage efficiency up to 1.64 % and 51.6 %, respectively.

Figure 2. Planar-shaped integrated DSSC and supercapacitor devices. a) Schematic illustration of a planar-shaped integrated DSSC and supercapacitor device based on multi-walled CNTs films and b,c) Photocharging and galvanostatic discharging curves of integrated devices with bare multi-walled CNT sheets and multi-walled CNTs/PANI composite films as electrodes, respectively. Reproduced with permission.^[88] d) Schematic illustration and optical photos of the integrated DSSC and supercapacitor device. e) The overall photoelectric conversion and storage efficiency of the integrated device versus the photo-charge time. Reproduced with permission.^[30]

It is well known that the output voltage of aqueous supercapacitors is usually lower than 1.5 V when they are integrated with solar cells. This cannot meet the requirements of future high-performance electronic devices. In order to achieve higher output voltage, the multifunctional devices can be connected in series, or alternatively by replacing with LIBs or organic supercapacitors.^[30] Wang et al. designed a multifunctional configuration with DSSC part on the top and LIB part on the bottom. The sharing electrode consisted of aligned TiO₂ nanotube arrays grown on both sides as the working electrode for DSSC part and the anode for LIB part.^[82] Electrons would be excited from the dye molecules and immigrated through the Ti foil to the anode part of the LIB. The corresponding holes would be accumulated at the counter electrode. The involved reactions at the anode of LIB could be expressed as follows:

Meanwhile, at the cathode side, the lithium ions deintercalated from the electrode via the following redox reaction:

Afterwards, the released electrons returned to the counter electrode of the DSSC part through the external circuit to combine with the holes at the counter electrode. In this case, the voltage of a single DSSC device was about 0.8 V when exposed to the sunlight. To ensure enough voltage to drive the LIB part, three tandem dye-sensitized solar cells, each of which consisting of two secondary dye-sensitized solar cells in series, were introduced to provide an open-circuit voltage of 3.39 V with a short-circuit current density of 1.01 mA cm⁻². The LIB could be charged to 3 V in 8 min and the discharge capacity of the power pack was about 38.89 μAh under a discharge current density of 100 mA g⁻¹ (**Figure 3**). A conversion efficiency of 0.82 % was obtained for the entire device and the efficiency of energy storage part was about 41 %. Additionally, red light-emitting diode (LED) lights could be effectively driven by the integrated device, revealing its potential as the power sources for future smart electronics. The DSSC-LIB devices have advantages over DSSC-supercapacitor systems such as higher output voltage and larger capacity. But since LIBs generally have significantly low power densities, they require longer charging time than supercapacitors. This problem is circumvented tactfully by using fiber-shaped hybrid energy storage devices.^[94] For example, Peng and co-workers reported a new family of in-series fiber-shaped electrochemical capacitors that could provide a high output voltage up to 1000 V.^[95] Such fiber-based energy storage devices may be further integrated with solar cells to realize self-power functions.

Figure 3. Planar-shaped integrated DSSC and LIB device. a) Schematic illustration of the device structure and working mechanism of a solar cell and Li-ion battery integrated device. SEM images of b) a vertically anodized TiO₂ nanotube array fabricated on Ti foil and c) on the FTO-coated glass. d) The discharge/charge cycling curves of the integrated device with four tandem DSSC units and one LIB unit. e) The LED lights powered by using the storage energy. Reproduced with permission.^[82]

Despite great progress, the above planar-shaped devices are generally rigid and in large sizes. Certain applications in future smart electronics require the power devices tailorable. Recently, fibre-shaped energy devices have been extensively developed for applications in portable and wearable electronics due to their flexibility, light weight and weaving properties.^[81, 96-98] The explored fibre-shaped energy devices mainly contain secondary energy harvest and storage devices.^[79, 81] Integrating fiber-shaped supercapacitors/LIBs with solar cells to form fiber-shaped integrated energy devices can realize self-power and portable applications simultaneously. A twisted fiber composed of both DSSC and supercapacitor unit has been reported by Chen et al. as demonstrated in **Figure 4a-g**.^[99] In this structure, a titanium wire with aligned TiO₂ grown on the surface was utilized as the sharing electrode and two aligned CNT fibers were intertwined on the titanium wire to generate the DSSC and supercapacitor system forming an integrated device. It was found that the TiO₂ arrays effectively provided enlarged contact area for electrodes and the twisted CNT fibers supported

the whole structure with an enhanced contact between the modified titanium wire with other parts. The entire device achieved an overall efficiency of 1.5 %, of which the power conversion efficiency was 2.2% and energy storage efficiency was about 68.4 %. In addition, Mai and coworkers developed a tailorable textile device with integrated functions of simultaneous solar energy harvesting (by ZnO-based DSSC) and storage (by TiN-based supercapacitor), which could be fabricated in a large scale and then woven into energy textiles. The supercapacitor could be charged by the DSSC to 1.2 V in 17 s, and interestingly, its charging rate could be adjusted by increasing/decreasing the length of the DSSC part.

Figure 4. Fibre-shaped integrated DSSC and supercapacitor devices. a) Schematic illustration of the integrated fibre-shaped device. b) Schematic illustration of the electrode connection during

charging and discharging. c) Photo charging/discharging curve of a fibre-shaped integrated device. Reproduced with permission.^[99] d) Schematics of the composition and structure (“thread to cloth”) of the integrated energy textile for future smart garments. e) Photographs showing the tailorability of the textile cloth which integrates DSSC and (fibre supercapacitors functions; f) equivalent circuit; g) light-charge and galvanostatic discharge performance. Reproduced with permission.^[50]

A coaxial fibre-shaped structure is capable of combining both advantages of fibre-shape and planar structure.^[79] Peng and co-workers prepared a modified bifunctional Ti/TiO₂ fiber with wrapped by aligned multi-walled CNTs not only as the counter electrode for DSSC, but also as electrode for supercapacitor (**Figure 5**).^[79] This “energy fiber” could simultaneously realize both energy conversion and storage. The photoelectric conversion and storage efficiency could reach up to 2.73 % and 75.7 %, respectively, with an entire efficiency of 90.6 % after 1000 hours. Therefore, such new architecture proves superior to the simple twisting structure in the fiber-shaped device.

Figure 5. Fibre-shaped coaxially integrated DSSC and supercapacitor devices. a) Schematic illustration of the structure of the coaxially integrated DSSC and supercapacitor into an “energy fiber”. b) Cross-sectional views of the DSSC and electrochromic parts of the “energy fiber”, respectively and optical photo of an “energy fiber”. c) Voltage and storage efficiency on the photo-charging time during the photo-charging and Galvanostatic discharging process and d) entire photoelectric conversion and storage efficiency on CNT thickness in the PC part on the photo-charging time. e) The entire photoelectric conversion and storage efficiency on the time. Reproduced with permission. ^[79]

2.1.2 Polymer solar cells (PSCs)-batteries/supercapacitors

Polymer solar cells (PSCs) have been gaining considerable research attention due to their unique advantages such as low specific weight, tunable material properties and low cost.^[85] A typical PSC is composed of a transparent layer of conductive indium tin oxide (ITO) cathode, a low work function metal anode, and an interlayer consisting of a conjugated polymer donor and a fullerene derivative acceptor. The cathode is generally modified by poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) or other n-type metal oxides or metal carbonates. In recent years, the mainstream structure for the interlayer of a PSC is the bulk heterojunction (BHJ) configuration, which is proven to be the most effective strategy to increase the interface area between the donors and acceptors, and realize an efficient charge separation.^[100, 101] Since the introduction of donor-acceptor bilayer heterojunction to the organic photovoltaic cell by Tang in 1979,^[102] great progress has been continuously achieved. The power conversion efficiency of PSCs is now approaching 10 %.^[103]

It is a consensus that advanced all-solid-state devices is the future trend of portable electronics.^[104-106] PSCs are expected to be an attractive candidate to meet the above requirements due to the offered possibilities of being free of liquid electrolyte. In this regard, all-solid-state multifunctional devices consisting of PSCs and supercapacitors are entering into people's vision. Chien et al. have reported a power device combining series connected PSCs with ~5 V open-circuit voltage and supercapacitors printed on the same substrate using graphene electrodes.^[80] As shown in **Figure 6**, the PSC part was assembled by using PEDOT:PSS modified ITO as cathode, poly(3-hexyl thiophene):phenyl-C₆₀-butyric acid methyl ester as active layer and aluminum as anode. Eight PSCs were connected in series and linked with a graphene-based supercapacitor device. Under continuous illumination, the series connected PSCs showed J_{sc} of 5.78 mA cm⁻², V_{oc} of 4.91 V, FF of 44.3 % and with a calculated photo conversion efficiency of 1.57 %. The voltage of the supercapacitor was charged to 3.8 V in 10 min under AM 1.5 illumination and the energy density was about 0.2 J g⁻¹ according to the discharging process. The designed device could easily power red, green, and blue LEDs. A printable all-solid-state photo-supercapacitor was reported using single-walled CNTs networks as a common integration platform between the PSC and the supercapacitor.^[86] The CNT network acted as an integration platform and the electrode of the supercapacitor was fabricated by the drop-casting of CNT solutions on top of the cathode (Al).

The hybrid architecture had the advantages of low thickness and light weight. Meanwhile the internal resistance of the device was 43 %, which was lower than that of the device where the PSC and supercapacitor were connected by an external wire.

Figure 6. Planar-shaped integrated PSC and supercapacitor device. a) Photograph and b) schematic illustration of a standard graphene based integrated-power-sheet device. Electrochemical characterization of 2 series connected graphene ink supercapacitors. c) The dynamic voltage-time plot during photo-charging and galvanostatic discharging process (0.3 mA). d) Charged power sheet was used to drive LEDs. Reproduced with permission.^[80]

Nonetheless, planar rigid structure still cannot satisfy next-generation electronic devices, and a series of works have been devoted to investigating the integrated devices being flexible and light-weight. Zhang et al. have utilized titanium wire modified by aligned TiO₂ nanotubes

as the sharing substrate and the PSC part was sequentially coated with $P_3HT:PC_{61}BM$ and PEDOT:PSS on the surface, follow by wrapping a single layer of CNT sheet to form the PSC part to achieve the best performance.^[90] As illustrated in **Figure 7**, one side was coated with CNT sheet and a layer of poly(vinyl alcohol) (PVA)/ H_3PO_4 gel electrolyte forming the supercapacitor part. For this architecture, the overall energy conversion and storage efficiency were highly sensitive to the thickness of the CNT sheet in the supercapacitor unit. A maximal overall efficiency of 0.84 % was achieved with a CNT sheet thickness of 20 μm . Furthermore, this all-solid-state fiber-shaped device exhibited high mechanical resistance and electrochemical stability. Moreover, the performance can be well maintained even after bending for thousands of cycles.

Here, we have summarized the main progress concerning the smart integration of solar cells and energy storage devices. As shown in Table 1, most of the integrations are modes I and II. Development of smart configuration in model III is desirable, of which the energy conversion and storage units are connected more effectively. In addition, fiber-shaped textile devices may be an important avenue to meet future wearable electronics. For whatever device architecture, both energy conversion and storage parts, the electrodes materials are always the key to achieve high performance.

Figure 7. Fibre-shaped coaxially integrated PSC and supercapacitor devices. a) Schematic illustration of the structure of an all-solid-state, coaxial, and integrated fiber device. b) Photo charging-discharging curve at a discharging current of 0.1 mA. The light illumination was 100 mW cm^{-2} . Reproduced with permission.^[90]

Table 1. A summary of solar cells and electrochemical energy storage integrated devices.

Integrated devices	Mode	Shape of device	Cs	$\eta_{overall}$	Ref.
DSSCs and Supercapacitor	II	planar	0.52 F cm^{-2}		[57]

DSSCs and Supercapacitor	II	twisted fiber	0.60 mF cm ⁻²	1.50%	[99]
DSSCs and Supercapacitor	II	Planar	1.4 mWh kg ⁻¹	/	[89]
DSSCs and Li-ion battery	II	Planar	8.3 mAh g ⁻¹	0.1%	[107]
DSSCs and Supercapacitor	II	coaxial fiber	3.32 mF cm ⁻²	2.06%	[79]
DSSCs and Supercapacitor	II	Fiber	41 mF cm ⁻²	2.12%	[81]
DSSCs and Supercapacitor	I	planar	6.5 F cm ⁻²	0.6%	[84]
DSSCs and Supercapacitor	II	Planar	1.29 mF cm ⁻²	1.64%	[30]
DSSCs and Supercapacitor	II	Planar	83 F g ⁻¹	0.79%	[88]
DSSCs and Supercapacitor	II	Fiber/textile	Tunable	0.9%	[50]
DSSCs and Li-ion battery	II	planar	38.89 μ Ah /device	0.82%	[82]
PSCs and Supercapacitor	I	planar	2.5 mF cm ⁻²		[80]
PSCs and Supercapacitor	II	Planar	28 F g ⁻¹		[86]
PSCs and Supercapacitor	II	Fiber	0.077 mF cm ⁻²	0.82%	[90]
Perovskite solar cells and Li-ion battery	I	Planar	142.1 mAh g ⁻¹ (0.1 C)	7.8 %	[90, 108]

2.2 Multifunctional electrochromic batteries/supercapacitors

In recent years, electrochromic energy materials have aroused great attention due to their combined properties of energy storage and optical modulation.^[14, 15, 109, 110] They can be able to change the optical properties persistently and reversibly by an external voltage. Their color evolution is affected by different redox states (faradic processes).^[111-116] Meanwhile, interestingly, the process of color change (optical modulation) in the electrochromic layer is

accompanied by energy storage/release related to the same electrochemical redox reactions.^[117-119] It is revealed that the electrochromic charge storage/release process can be indicated by the color change and quantitatively monitored by the optical transmittance. In the light of this unique property, electrochromic energy materials are the main component for smart windows, which are widely used in modern buildings, sport cars and airplanes. Similarly, electrochromic energy materials can also be combined with solar cells and thermoelectric material (thermal energy) to further enhance the utilization of total energy.^[120]

Figure 8. Electrochromic supercapacitors. a) Schematic illustration of a supercapacitor based on two laterally offset double-gyroid structured electrodes. b) Photograph of a transparent electrochromic supercapacitor. Scale bar, 1 cm. Reproduced with permission.^[121] c) Photographs of the supercapacitor electrode at different states to demonstrate the stored energy conveyed through the patterned color scheme. Reproduced with permission.^[122]

An interesting work of Wei et al. adopted an ordered bi-continuous double-gyroid V_2O_5 network as both electrochromic and energy storage materials to fabricate an electrochromic supercapacitor.^[121] As shown in **Figure 8a-b**, during color variation process between yellow/green, the V_2O_5 reacts with Li^+ to form LiV_2O_5 through a two-stage redox reactions:

The obtained electrochromic supercapacitor devices based on double-gyroid V_2O_5 exhibited fast electrochromic switching time and higher chromatic contrast than its non-templated counterpart due to its improved reaction kinetics with faster ion/electron transfer. The electrochromic supercapacitor showed an energy density of 52 Wh kg^{-1} at 1 kW kg^{-1} . Furthermore, even at high power density of 16.7 kW kg^{-1} , the multifunctional electrochromic supercapacitor could still achieve an energy density as high as 13.9 Wh kg^{-1} . Similar electrochromic supercapacitor could be realized by using WO_3 family. Zhao and co-workers fabricated a novel electrode of electrochromic supercapacitor and demonstrated that the color changes could be used to monitor the levels of energy (**Figure 8c**). $W_{18}O_{49}$ and PANI were applied as chromatic active materials to constitute the pattern and background in this device, and their operated potential windows were in the range of -0.5 to 0 V and 0 to 0.8 V , respectively. This combination could remarkably broaden the voltage window up to 1.3 V . The variations in color schemes depends on the level of energy storage. Similarity, Peng and co-workers developed stretchy and flexible smart electrochromic supercapacitor by depositing PANI onto aligned carbon nanotube (CNT) sheet electrodes and enhanced performance was verified in this system.^[90]

It is essential to design and fabricate large-scale electrochromic devices to meet the requirements of practical application. Yang et al. designed an electrochromic supercapacitor with a size of $15 \times 15 \text{ cm}^2$ by using WO_3 -based materials.^[123] This electrochromic supercapacitor exhibited an optical transmittance of 78.8% at the bleached state and 15.1% at the colored state at 633 nm , corresponding an optical transmittance change of 63.7% . An encouraging specific capacitance of 160.1 F g^{-1} at 0.4 mA cm^{-2} was also achieved in this device configuration, and over 95% of the initial capacitance could be retained after 5000 cycles. Additionally, it has been reported that silver grids are promising conductive substrate to replace ITO as flexible transparent conductors. Lee and coworkers developed a flexible electrochromic device based on silver grid supported WO_3 nanoparticles/PEDOT:PSS hybrid film.^[124] A large optical modulation of 81.9% at 633 nm and high coloration efficiency of $124.5 \text{ cm}^2 \text{ C}^{-1}$ was achieved in this system. Furthermore, the electrochromic supercapacitor exhibited a specific capacitance of 221.1 F g^{-1} at 1 A g^{-1} , and it can deliver 48.6 F g^{-1} at a high current density of 10 A g^{-1} , revealing the potential as promising candidate for future optoelectronic devices.

Prussian analogues, one family member of electrochromic active materials, have been utilized in an electrochromic self-rechargeable battery reported by Wang et al.^[125] In this work, aluminum was used to reduce Prussian blue (PB) (blue in color) to Prussian white (PW) (colorless) in potassium chloride electrolyte (see **Figure 9**). The capability of self-charging was realized by simply disconnecting the aluminum and PW electrodes, which would be spontaneously oxidized from PW to PB by the dissolved oxygen in aqueous solution. Nevertheless, the coloration time in this system was very slow up to 4 h, suggesting that it was not suitable for practical application. To further improve the processing technique of electrochromic supercapacitors, in recent years, Cai et al. have developed a facile inkjet printing method to prepare WO₃/PEDOT:PSS and CeO₂/TiO₂ films. The inkjet printing method is a precise and noncontact coating technology with the advantages of low cost and high-resolution patterns. In this case, inkjet printed WO₃/PEDOT:PSS and CeO₂/TiO₂ films were assembled to fabricate the multifunctional smart window.^[126] The switching time of the device was 12.7 s for coloration and 15.8 s for bleaching, respectively. Moreover, it remained a transmittance modulation of 76.7% of the first value after being tested for 200 min, demonstrating its excellent electrochemical stability.

The smart electrochromic devices can be able to change color, thus making it possible to control the solar radiation transmittance through windows. Meanwhile, they can also store the energy for later use. For example, the stored energy can be used to light the building and power other electronic devices. Fortunately, it is very attractive to integrate energy harvest system with the smart electrochromic devices to endow them with more functionalities to satisfy more demands. In view of low cost and facile processing, dye-sensitized solar cells are firstly combined with the electrochromic devices. In order to provide sufficient voltage to drive the electrochromic parts, Ahn et al. developed tandem DSSC devices with two-faced transparent conducting oxide, where the dye-sensitized solar cells were assembled with 7 nm-thick TiO₂ and 4 nm-thick Pt layers.^[10] Under 1.5 AM illumination, the connected solar harvest demonstrated an open circuit voltage of 1.35 V and short circuit current density of 3.96 mA cm⁻², respectively. Furthermore, an encouraging switching time of 60 s for coloring

Figure 9. Self-powered electrochromic battery. a) Optical photo of the as-prepared electrochromic device. (b) The bleached state by connecting the PB and Al electrodes. c) Schematic illustrations of functioning mechanisms for the bi-functional device. Reproduced with permission.^[125]

and 45 s for bleaching process is obtained, respectively. It is indicated that this combination is feasible and improve the energy utilization efficiency. However, the cell efficiency and close-circuit current of the above integrated device were relatively low due to its complicated configuration. In this regard, two different types of integration of self-powered smart windows based on WO_3 film as electrochromic electrode and DSSC as power supply were designed and studied by Chen and coworkers.^[127] As shown in **Figure 10**, for the device I, the smart window consist of an independent electrochromic device and a DSSC device, which

could power the former to control the coloration and bleaching states. For the device II, the smart window has an integrated configuration with combined electrochromic device and a DSSC device. This configuration is more effective in energy utilization and color modulation with faster response time and color contrast as well as a high coloration efficiency of $61.6 \text{ cm}^2 \text{ C}^{-1}$.

Figure 10. Planar-shaped integrated DSSC and electrochromic device. Schematics of a DSSC driven electrochromic smart window under illumination of sunlight: circuits of (a) the independent device (Type I) and (b) the assembled integrated device (Type II). Reproduced with permission.^[127]

Over recent years, different solar cells have also been utilized as power source for the integrated smart windows. Typically, perovskite solar cells based on methyl-ammonium lead halide ($\text{CH}_3\text{NH}_3\text{PbX}_3$, $\text{X} = \text{I}, \text{Cl}$ or Br) have been extensively investigated due to advantages of high efficiency (up to 15-21 %), low cost and simple fabrication techniques.^[128, 129] It is reported that fully printable perovskite solar cells based on $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ hetero-junctions and cheap carbon counter electrodes are particularly compatible with electrochromic glass in smart windows. Recently, our group designed and fabricated solid-state electrochromic batteries powered by perovskite solar cells (**Figure 11**).^[18] The solid-state electrochromic batteries consisted of a reduced graphene (rGO)-connected bilayer NiO nanoflake array cathode and a WO_3 nanowire array anode. The perovskite solar cell was fabricated by coating with two layers of TiO_2 on FTO, followed by successive depositing of a ZrO_2 spacer layer of 1 mm, a mesoscopic carbon layer and dipping 5 ml of $\text{CH}_3\text{NH}_3\text{PbI}_3$

precursor at the end. Under continuous illumination, a single perovskite solar cell could produce a voltage of ~ 0.89 V with a maximum current density of ~ 18 mA cm $^{-2}$. The overall coloration efficiency of the device was measured with about 135.5 cm 2 C $^{-1}$. It is noteworthy that the conversion process was fast with a switching time of 2.5 s for coloring and 2.6 s for bleaching process, superior to other reported solid-state electrochromic devices.^[51]

Figure 11. Planar-shaped integrated perovskite solar cell and electrochromic device. a) Schematics of the device structure and working principle of the combined devices. b) Photos of different samples of a perovskite solar cell and solid-state electrochromic battery. c) Transmittance spectra of the solid-state electrochromic batteries in the visible and near-IR region (400-2000 nm) at bleached and colored states (photos of the electrochromic batteries at different states in insets). d) Voltage-time responses of the solid-state electrochromic batteries during the charged and discharged processes. Reproduced with permission.^[18]

2.3 Multifunctional tribological generator- batteries/supercapacitors

Mechanical energy, such as vibrational and frictional energy, is another ubiquitous energy resource that can be converted and stored as electrical energy. Among the explored various conversion routes, triboelectric nanogenerators (TENG) attract the most attention toward

harvesting of available mechanical energy in the environment, including wind, ocean waves and human motion.^[130] Similar to solar energy, the mechanical energy is also considered as intermittent source of energy due to the irregular and recurrent characteristics. Hence, it is necessary to store and accumulate the converted electrical energy in EES for later applications.

Figure 12. Wearable integrated triboelectric nanogenerators and LIB device. a) Schematic illustration of fabrication of TENG-cloth. b) An optical image of the integrated self-charging power system that harvests mechanical energy of human motion with TENG-cloth, stores the energy with LIB belt, and then powers heartbeat meter strap. c) The equivalent electrical circuit of the self-charging power system. d) The voltage profiles of the LIB belt charged by the TENG-cloth.

Since the discovery of TENG by Wang group,^[130] great progress has been achieved in the fundamental mechanisms of TENG as well as the development of self-powered devices. The working mechanism is based on the conjunction of triboelectrification and electrostatic effects *via* two materials with significantly different tribo-polarities. One electrode is easily able to gain electrons, while the other requires to lose electrons easily. Compared with other energy conversion systems, the fabrication process of the triboelectric nanogenerators is facile and cost-effective. Additionally, the triboelectric nanogenerators can produce a high output power, which is important for the portable electronics. But the collected current from a sing-step friction is very small. For instance, Wang and coworkers integrated a TENG with a flexible supercapacitor to form a wearable self-charging power device.^[131] A rGO modified polyester yarn supercapacitor was prepared for the energy storage combined with a TENG fabric woven. The two parts were finally combined by weaving them to form an individual TENG-supercapacitor power textile. The three-series yarn supercapacitor could be charged by the TENG cloth to 2.1 V in 2009 s with a vibration motor at about 5 Hz and could be then discharged at 1 μ A for 811 s, further confirming the validity of this smart device. Similarity, LIBs can be effectively integrated with triboelectric nanogenerators as well. Pu et al. has developed a wearable device consisting of a triboelectric nanogenerators cloth and a LIB belt with a rectifier. The generated current was produced by human motion energy and could be directly stored by the combined LIB. The LIB was charged rapidly to about 1.9 V by the TENG cloth at low-frequency motions and provided sufficient energy output to power small electronics such as heartbeat meter. It is interesting that the textile TENG-cloth could be weaved at many different positions of the human body because of its versatility in scavenging energies of various modes of human motions as well as excellent flexibility and stable electrochemical performance, thus broadening its potential applications as smart wearable electronics. Furthermore, higher energy generation could be expected when the wearer was doing strenuous exercises.^[132]

3. Challenges and Prospect

Integrated multifunctional devices with different functions are becoming part of the emerging smart technologies. In particular, it is of great importance to integrate energy systems with other functions to reduce the fabrication/maintenance cost and maximize the performance. Energy harvest/generation and storage technologies are closely bound up with each other. It is incontrovertible that energy storage and conversion technology and corresponding materials are becoming the research mainstream in recent years, and have therefore triggered extensive interest in developing advanced multifunctional systems associated with energy materials. To take full advantage of energy harvest and storage, organic combination of both functions is highly desirable. In the past decade, this combination has proven to be an effective way to fabricate high-performance wireless and self-powered devices. Particularly, multifunctional smart windows with electrochromism and energy storage could maximize the utilization of solar energy and reduce the cooling/heating load of modern building. Moreover, some other smart devices including remote sensors and wearable electronics are also integrated with energy harvest components to realize self-power for a long duration without maintenance.

Despite the enormous progress made in designing and fabricating multifunctional devices, their current performances are still far from satisfaction and could not meet the growing demand of next-generation electronics. On one hand, the structure of integrated energy harvest and storage devices needs further optimization. Nowadays, most of the integration modes, taking PSC as an example, are generally confined in modes I and II, where the energy conversion and storage units are connected via an external circuit or connected via an internal integration platform. This combination causes inevitable energy loss and low energy utilization. Hence, it is highly necessary to develop smart configuration in the mode III, that is, the energy conversion and storage units are sharing both the electrode and electrolytes, by which the smart devices can deliver the same functionalities but with simpler and smaller structure, thus making the combination more effective. On the other hand, improving the overall performance and reducing the fabrication cost are two key factors to extend the practical smart electronics. Integrated devices with cost-effective raw materials, facile fabrication and simply packaging structures are preferred. Meanwhile, whether energy conversion and storage devices, electrodes based on new and advanced active materials is the key to achieve the enhancement in performance and sustainability. Additionally, to satisfy the requirements of the future smart electronics, tailored structures such as fibre-shape, stretchy configuration and woven characteristics are desirable to be developed. This is a highly interdisciplinary topic that requires cooperation of researchers with complimentary expertise.

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TOC entry

Marriage for better life. This Review summarizes the latest advances in the integrated/joint smart multifunctional energy devices, with a focus on electrochromic batteries/supercapacitors and solar cells + batteries/supercapacitors. The design concepts and their merit/demerits are discussed.

Keywords: Integrated energy devices; Solar energy conversion; Batteries; Supercapacitors; Electrochromics

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Integration of energy harvesting and electrochemical storage devices