Conjugated Polymers for Flexible Energy Harvesting and Storage

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Since the discovery of conjugated polymers in the 1970s, they have attracted considerable interest in light of their advantages of having a tunable bandgap, high electroactivity, high flexibility, and good processability compared to inorganic conducting materials. The above combined advantages make them promising for effective energy harvesting and storage, which have been widely studied in recent decades. Herein, the key advancements in the use of conjugated polymers for flexible energy harvesting and storage are reviewed. The synthesis, structure, and properties of conjugated polymers are first summarized. Then, their applications in flexible polymer solar cells, thermoelectric generators, supercapacitors, and lithium-ion batteries are described. The remaining challenges are then discussed to highlight the future direction in the development of conjugated polymers.

1. Introduction

1.1. Conjugated Polymer

The great potential of conjugated polymers (CPs) in various applications ranging from electronics, aerospace, sensing, catalysis and energy to biomedicine is one of the main reasons for the intensive investigation of these materials. The first CP, polypyrrole (PPy), was found in the 1960s but with little understanding.[1] Until 1977, the electrical conductivity of polypyrrole (PA) found by MacDiarmid and co-workers was dramatically enhanced by several orders after doping with iodine, which greatly reattracted the interest of researchers toward the investigation and progress of new CPs.[2,3] Since then, the number of CPs was explosively increased, mainly including polythiophene (PT), poly(3,4-ethylenedioxythiophene) (PEDOT), poly(para-phenylene), poly(phenylenevinylene) (PPV), polyfluorene, and polyaniline (PANI), the structures of which are shown in Figure 1.[4]

Typically, CPs can be synthesized by chemical or electrochemical methods. Traditional chemical synthesis is composed of condensation and addition polymerization, which provides various accessible and effective routes to prepare a wide range of CPs. Electrochemical synthesis is carried out with a three-electrode system including working, counter and reference electrodes inserted in a mixed solution of monomer, solvent, and electrolyte. CPs are then deposited on the working electrode with the electrical current passed through the solution. Compared to the traditional chemical synthesis, electrochemical synthesis is a preferred alternative for preparing CPs regarding its reproducibility and simplicity, in addition to several novel CPs with modified monomers or complex structures.

CPs exhibit nearly no conductivity before doping. After doping, their electrical conductivity was significantly improved by several orders of magnitude for the formation of charge carriers.

During the oxidation and reduction processes of the neutral polymer, the electron was localized to generate the polaron, and this polaron is easier to lose the second electron to form bipolaron than that of other parts in the polymer chain.[5] The electrical conductivity of CPs can be determined by a series of factors such as the polaron length, conjugation length, and entire chain length.

Generally, polymer-based materials exhibit high flexibility due to the nature that their polymer chains can spontaneously change their conformations via internal rotations among single bonds.[6] Besides, their flexibility could be increased with the increasing temperature below their glass-transition temperatures. Compared to flexible polymers, the flexibility of CPs is relatively low due to the conjugated structure in their polymer chains. However, the flexibility of CPs is high enough for applications in flexible energy devices compared to the nonpolymer based materials. The flexibility can be characterized by the barrier to internal rotation, conformational entropy, polymeric segmental length, and mean square end-to-end distance.[7,8]

1.2. Flexible Energy Harvesting and Storage Device

Global energy demand is increasing significantly, and great deals of efforts have been made to develop new materials to accelerate the advancement of energy-related technologies. In the past decades, energy harvesting and storage devices are witnessing a rapid development. Organic solar cells have achieved a milestone where the maximal power conversion efficiency (PCE) of them exceeds 10%;[9] the new emerging perovskite solar cells have reached a maximal PCE of above 20%;[10] the PCE of Si solar cells exceeded 45%;[11] the power densities of thermoelectric generators based on Bi₂Te₃...
reached nearly 60 μW cm−2 under indoor conditions;\textsuperscript{[12]} the metal oxide-based supercapacitor realized specific capacitance of 2244 F g\textsuperscript{−1};\textsuperscript{[13]} a high specific capacitance of over 800 F g\textsuperscript{−1} is achieved by using the nitrogen-doped ordered mesoporous few-layer carbon as the electrode of supercapacitors;\textsuperscript{[14]} the energy density of lithium-ion batteries (LIBs) based on Li\textsubscript{i+M} (M = Si, Sn, or Al) graphene anodes reached around 490 Wh kg\textsuperscript{−1};\textsuperscript{[15]} LIBs that can self-heat at low temperatures have been developed to remarkably improve the availability of applications including electric cars in cold climates and high-altitude drones with high efficiencies.\textsuperscript{[16]} With the great progress in performances of energy harvesting and storage devices, scientists are engaging in improving their mechanical malleability that enables them potential for the scalable roll-to-roll printing technology\textsuperscript{[17–23]} and compatible with flexible or nonplanar substrates so as to extend their applications, for example, portable and wearable electronic technologies.\textsuperscript{[24–26]}

Recently, flexible energy harvesting and storage devices have witnessed a tremendous development mainly owing to the dramatic innovation of flexible electronic materials, particularly, CPs. CPs with high physical properties such as high electrical conductivity, good tensile strength, high flexibility and light weight, and excellent chemical properties such as fast kinetics of oxidation/reduction reaction are promising for constructing flexible energy harvesting and storage devices. Typically, these flexible devices are first fabricated on flexible substrates such as poly(ethylene terephthalate), poly(dimethylsiloxane), polyurethane, textile, and cloth on the basis of layer-by-layer coating processes and then encapsulated by the barrier materials. The physical properties of the typical CPs, polymer substrates, and barrier materials are summarized at Table 1.\textsuperscript{[27–31]} The mechanical properties such as elastic modulus, Poisson’s ratio, toughness, and thermal expansion coefficient, of the CPs are critically important for the realization of flexible devices.\textsuperscript{[32–34]} Although a lot of polymers have been explored, it is rare to provide quantitative standards or ranges where the devices can be made flexible. The flexibility of the devices may be characterized by tracing the main performance parameter of device under repeated bending with varying angles. For instance, a flexible solar cell was reported to maintain over 90% photovoltaic conversion efficiency after bending for 1000 cycles at a bending angle of 180° without sealing,\textsuperscript{[29]} while the supercapacitor showed 94% storage efficiency after bending for 1000 cycles at bending angle of 180°.\textsuperscript{[31]} Since the dimension of devices being tested varies, the flexibility obtained under the same bending angle is not comparable in terms of devices of different structures and sizes. Regulating the radius of curvature of the bending process might be more accurate while it is rarely adopted by now. Besides, no clear quantitative definition has been made on when a device may be named flexible or not, and it is also unavailable for quantitative comparisons on their flexibility either. Neither do the devices based on inorganic materials. Systematic studies are needed to provide quantitative comparisons and standards to characterize the flexibility in the future. In the following parts, we will focus on the recent progress in using CPs for flexible energy harvesting and storage devices including polymer solar cells (PSCs), thermoelectric generators, supercapacitors, and LIBs.

2. Conjugated Polymer for Flexible Energy Harvesting

Typically, flexible energy harvesting devices are mainly composed of PSCs and thermoelectric generators. In these devices, electrodes and active materials are critically important, which are usually required to be electrically conductive and mechanically flexible. Besides, the active materials must possess the property of semiconductor so as to form heterojunction in active...
layer. All abovementioned properties are matched by the CPs that have boosted the development of flexible PSCs and thermoelectric generators.

### 2.1. Polymer Solar Cell

Solar energy being accepted as an alternative for fossil fuel has already dominated a commanding lead in a wide range of research fields. Flexible PSCs can be readily achieved on the flexible polymer substrate through a series of scalable printing techniques such as inkjet, doctor blade, and roll-to-roll processes. These make them the most desirable alternative for lightweight, low-cost, solution-processable, and flexible photoelectric conversion devices compatible with industrial mass production. The PCEs of flexible PSCs have been improved as high as 9.4%,[35–37] which prospects a bright future for their applications in flexible energy-harvesting integrated systems.

#### 2.1.1. Working Mechanism

Originally, PSCs were achieved by the introduction of the donor–acceptor bilayer planar heterojunction. However, this planar heterojunction design possesses many limitations such as the low interface area between the donor and acceptor, and the need of long carrier lifetime that enables the excitons to be effectively separated. All these issues can be addressed with the help of a bulk heterojunction that involves mixing donor–acceptor materials in the photoactive layer. Nowadays, the bulk heterojunction is the most popular structure in the area of PSCs with high performance and mechanical flexibility.

The working mechanism of PSCs with a bulk heterojunction is indicated in Figure 2a.[38] The energy harvesting process is described below: (1) absorption of light with the generation of excitons, (2) diffusion of the excitons, (3) dissociation of the excitons with the generation of charge, and (4) charge transport and collection. The PCE (\(\eta\)) of PSCs is calculated by dividing the maximum output power with incident power

\[
\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{J_{\text{SC}} \times V_{\text{OC}} \times FF}{P_{\text{in}}}
\]

Here \(J_{\text{SC}}\) is the short-circuit current density, which is equal to the integral of the overlapping part between solar spectrum and cell responsivity (Figure 2b); \(V_{\text{OC}}\) is the open-circuit voltage, which is mainly determined by the energy level difference

| Table 1. Physical properties of typical CPs, polymer substrates, and barriers. |
|-----------------------------|-----------------------------|-----------------------------|
| Material \[a\] | Type | Conductivity | Mechanical properties | Contribution |
| PA | Conducting/semiconducting | \(1.70 \times 10^{11}–3.8 \times 10^{2} \text{ S m}^{-1}\) | Bendable (in a nanocomposite film)\[27\] | Active material and electrode material |
| PPy | Conducting | \(0.02–1 \text{ S m}^{-1}\) | No difference upon application of 13% bending strain (in a planar supercapacitor)\[28\] | Active material and electrode material |
| PEDOT | Conducting | \(550–1000 \text{ S m}^{-1}\) | Slightly decreased after bending for 1000 cycles (in a fiber-shaped PSC)\[29\] | Active material and electrode material |
| PPV | Conducting | \(10^{1}–1 \text{ S m}^{-1}\) | Bendable (in an organic planar solar cell)\[30\] | Active material and electrode material |
| PANI | Conducting/semiconducting | \(6.3 \times 10^{-2}–4.6 \times 10^{-3} \text{ S m}^{-1}\) | Well maintained after being stretched for 100 cycles to a strain of 100% (in a fiber-shaped supercapacitor)\[31\] | Active material and electrode material |
| PET | Insulating | – | Elongation at breaking > 50%; Young’s modulus of 2.8–3.1 GPa | Substrate and flexible barrier |
| PDMS | Insulating | – | Elongation at breaking > 200%; Young’s modulus of 0.01–0.07 GPa | Substrate and flexible barrier |

\[a\] PA: polyaniline; PPy: polypyrrole; PEDOT: poly(3,4-ethylenedioxythiophene); PPV: poly(phenylenevinylene); PANI: polyaniline; PET: poly(ethylene terephthalate); PDMS: poly(dimethylsiloxane).
between the lowest unoccupied molecular orbital (LUMO) level of acceptor and the highest occupied molecular orbital (HOMO) level of donor; FF is the fill factor, which is defined by the following equation, indicating the similarity of the shape of $J-V$ curve to the rectangular

$$FF = \frac{J_{max} \times V_{max}}{J_{SC} \times V_{OC}}$$

The parameters for the performance of PSCs including $V_{OC}$, $J_{SC}$, and FF are determined by the intrinsic properties of the photoactive and charge-extracting CPs as well as device architectures. It is obviously that a broader solar spectrum and a greater energy level difference between the LUMO level of acceptor and the HOMO level of donor will contribute to high values of $J_{SC}$ and $V_{OC}$. However, it remains a challenge to enhance both of them simultaneously. This is because narrowing the bandgap can improve $J_{SC}$, however, resulting in the decrease in $V_{OC}$ due to the higher HOMO level. Therefore, a potential solution is compressing the bandgap to increase the $J_{SC}$ while lowering the HOMO level of donor polymer to enhance the $V_{OC}$. Both of them will be discussed in the following parts in combination with the FF.

2.1.2. Conjugated Polymer as Light Harvesting Material

The progress in flexible PSCs is usually accompanied with the discovery and design of new materials with high performances. Donor and acceptor materials are two key materials in the photoactive layer, determining the resultant PCEs of PSCs. Generally, p-type CPs are employed as the donor materials and then they are mixed with a kind of commercial acceptor material, typically [6,6]-phenyl-C$_{61}$butyric acid methyl ester (PCBM), to form the bulk heterojunction for photoelectric conversion. Recently, there have been also several studies on all-polymer PSCs by using CPs as acceptors, which will be introduced later.

**Donor Material**: Generally, the optimization of flexible PSCs requires the appropriate electronic properties of the donor and acceptor components to absorb light, generate excitons, and separate and transport charges with the lowest loss of energy. As the PCBM is the commonly used acceptor materials and then they are mixed with a kind of commercial acceptor material, typically [6,6]-phenyl-C$_{61}$butyric acid methyl ester (PCBM), to form the bulk heterojunction for photoelectric conversion. Recently, there have been also several studies on all-polymer PSCs by using CPs as acceptors, which will be introduced later.

The earliest donor polymer employed for bulk heterojunction is derived from the poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene) with the PCE approaching to 1%. However, this PCE is far from the expectation for practical applications and then many studies focused on further increasing PCEs of PSCs by optimizing the structure of donor materials. Soluble polythiophenes, in particular poly(3-hexylthiophene) (P3HT), has leaped as the standard donor polymer for PSCs because of its high hole mobility, broad spectrum coverage, and low cost. Many flexible PSCs have been constructed based on the P3HT:PCBM with the maximum PCE of 4.3%. One attractive work was fabricating the PSC on an ultrathin 2 µm thick poly(ethylene terephthalate) substrate to achieve a highly flexible PSC that can be wrapped around a human hair. This ultrathin PSC was further attached on a prestretched poly(dimethylsiloxane) substrate, so that, after releasing the poly(dimethylsiloxane) to the original state, the “buckles” were formed in this ultrathin PSC. Therefore, this PSC can be repeatedly stretched between the buckling and flat states. However, P3HT is not beneficial for achieving a higher PCE regarding its large bandgap and mismatched energy diagram level with acceptor material.
As the performances of PSCs are primarily determined by three factors of $V_{OC}$, $J_{SC}$, and FF, tremendous efforts have been made to design new CPs with suitable bandgaps and energy levels so as to achieve high performances. P3HT as the most commonly used donor has an electron-rich group with a relatively lower $V_{OC}$ of 0.6 V. In order to increase the $V_{OC}$, the
HOMO energy level of the donor polymer should be lowered by designing groups that are less electron-rich. For example, the CPs with the incorporation of fluorine substituent had lowered their HOMO energy level by as much as 0.29 eV compared to the nonfluorinated polymers. As a result, the $V_{OC}$ of the resultant PSCs was increased by 0.07 V for the difluorinated polymers. Furthermore, a higher $V_{OC}$ of 0.89 V was achieved by introducing carbazole units in the polymer chain of poly[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT). Recently, a designed polymer donor, poly(indaceno-dithieno[3,2-b]thiophene difluorobenzothiadiazole) (PIDTT-DFBT) with a deep HOMO level reached a $V_{OC}$ as high as 0.96 V with the maximal PCE as high as 9.4%. $J_{SC}$ is another determining parameter for a high-performance PSC. An effective strategy to achieve high $J_{SC}$ is to narrow the bandgap for a broader solar spectrum coverage. Many approaches were employed such as designing a suitable donor–acceptor structure, adjusting the conjugation length and controlling the polymer chain planarity. Among them, designing a suitable donor–acceptor structure is the most straightforward approach. For instance, a PSC with thiено[3,4-b]thiophene/benzothiophene (PTB7) as a donor polymer showed a PCE of 8.34% and was maintained by 96% even after 400 bending cycles. The characterization on the flexibility of the PSC was carried out by tracing the PCE variation under repeatedly bending and releasing at a specific bending angle. Here the PTB7 with the thiienothiophene unit modified by the fluorine atom exhibited both low HOMO and LUMO energy levels, and thus benefit for the high $J_{SC}$. With further optimization of the device structure to enhance optical absorption by matching the optical constants of the interlayer, the PCE reached 9.2%. The third parameter for achieving high PCE in a PSC is the FF, which is the ratio between the maximal obtainable power and the product of $J_{SC}$ and $V_{OC}$, being determined by several factors such as charge carrier mobility and balance, interface recombination, internal resistances and film morphology between the donor and acceptor. Up to now, there is not a clear understanding about the FF. For the material design, great efforts should be paid to the molecular chain including high-mobility units and crystallinity. Meanwhile, an inverted structure was verified to have a considerable effect on the FF, which was mainly ascribed to the vertical phase gradiation. Recently, an attractive tandem solar cell concept, which combines two or more subcells based on CPs with different absorption ranges, was employed to further improve PCEs by greatly enhancing photon utilization efficiencies. Here a representative tandem PSC fabricated in serial printing and coating processes is highlighted in Figure 5. In this work, a high $V_{OC}$ of 1.32 V was achieved but with a low PCE of 2.67% due to the low optical transparency of substrate and partly overlapped absorption spectrums from two tandem cells. However, considering the scalable fabrication for the tandem cell with 12 layers, the PCE is acceptable.

**Acceptor Material:** Although most studies on PSCs have involved the PCBM as the most popular acceptor, fullerenes still have some shortcomings, such as weak absorption in the visible region, difficult purification, and limited energy level variation. Moreover, the mechanical flexibility of PCBM-based PSCs awaits to be further improved. Therefore, nonfullerene acceptors, in particular polymer–acceptor materials, have attracted increasing attentions for easy modification and purification, tunable energy level and electronic properties, broad absorption and enhanced flexibility, which provided an encouraging boost in the development of flexible PSCs. The polymer–acceptor materials should contain the units that possess high electron mobility and affinity so as to promise the rapid charge separation and transport.
For instance, a PSC with a blend of poly[4,8-bis(5-(2-ethylhexyl) thiophen-2-yl)benzo[1,2-b:4,5-b]dithiophene-alt-1,3-bis(thiophen-2-yl)-5-(2-hexyldecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione] (PBDTTTPD) donor and poly[N,N′-bis(2-hexyldecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl-alt-5,5′-thiophene] (P(NDI2HD-T)) acceptor as a photoactive layer showed a PCE of 6.64%, which was higher than that of the PSC with PCBM as electron acceptor (6.12%).[61] Importantly, these all-polymer solar cells exhibited a better flexibility compared to that of PCBM-based PSCs, because the polymer donor can entangle with polymer chains of acceptor to form strengthened interfaces (Figure 6). The electronic property of all-polymer blend film exhibited a high stability in comparison with that of the PCBM-based blend film. The PCBM-based blend film generated obvious crack during repeatedly bending, leading to the performance degradation. Although the emergence of polymer acceptors provides guidelines for further design of PSCs with high flexibility, their electronic property and structure still should be optimized before using in PSCs.

2.1.3. Conjugated Polymer as Charge Transport Material

Typically, CPs can be employed as both a hole-transporting layer and a transparent conductive electrode to replace the rigid indium tin oxide electrode for flexible PSCs because of their high capability of hole extraction and transport.[62] Among them, PEDOT:poly(styrenesulphonate) (PSS) is the most investigated hole-transporting and electrode material, which is already commercialized with a series of commonly used types such as 4083, PH500, and PH1000. In many cases, PEDOT:PSS was used as both a hole-transporting layer and a conductive electrode to construct flexible PSCs through a full roll-to-roll processing on the flexible substrate.[63,64]

The electrical conductivity of PEDOT:PSS can be improved by mixing two types of PEDOT:PSS such as PH500 and 4083 due to the complementary properties of two PEDOT forms in conductivity and topography.[65] However, it is still far away for achieving high-performance PSCs. Therefore, many attempts have been made to enhance the electrical conductivity by optimizing their surface morphology with other solvents including hexafluoroacetone,[66] dimethyl sulfoxide (DMSO),[67,68] formic acid,[69,70] and isopropyl alcohol.[71] As a demonstration, the liquid-crystalline ionic liquids, e.g., 1-hexadecyl-3-methylimidazolium hexafluorophosphate, can also be employed to remove the insulating PSS on the surface of the PEDOT:PSS while making the remained PEDOT in a continuous state.[72] Besides, PEDOT:PSS can be composited with other highly conductive materials such as Cu nanowires,[73] Ag nanowires,[74,75] Ag grids,[64,76–78] and single-wall carbon nanotube (CNT)[79] to form composite electrodes for flexible PSCs by using high-throughput printing technologies. Based on this composite structure, CPs can provide the necessary work function with the electrical conductivity enhanced by the conductive components.

Although abovementioned PSCs exhibited high flexibility, they cannot meet the requirements for many unique applications, for example, textile technology. In textiles, PSCs were not only required to be flexible, but also twistable to adapt to the complex deformations in practical use. Therefore, a new family of fiber-shaped PSCs was developed by continuously dip-coating the PEDOT:PSS layer and wrapping the aligned CNT sheet or CNT fiber on the titania wire coated with the photoactive layer.[29,80] These fiber-shaped PSCs exhibited a good flexibility with the PCE maintained by nearly 90% after bending for 1000 cycles (Figure 7a,b). They can be further enabled to be stretchable by designing a spring-like structure so as to well suffer from the external stress (Figure 7c).[81]
Although great efforts have been made to weave these fiber-shaped PSCs into textiles, high-efficient PSC textiles were still not realized, due to the damage of PSC surfaces, short circuits caused in weaving processes, limited effective areas and low PCEs. A potentially effective strategy to solve these problems was directly fabricating the PSC on the textile-like electrode to form the PSC textile (Figure 7d). As expected, the resultant PSC textiles were flexible with PCEs changed by below 3% after bending for 200 cycles, which provided a big step toward applications in portable and wearable energy-harvesting systems.

The comparison of photovoltaic parameters in abovementioned PSCs is summarized in Table 2.[23,36,37,39,40,49]

It should be noted that CPs, e.g., PEDOT:PSS, can also be employed as counter electrodes or hole-transporting layers for flexible dye-sensitized solar cells[83–88] and perovskite solar cells,[89] respectively. Here, due to the limitation of length, we will not introduce them in detail.

2.2. Thermoelectric Generator

Apart from the PSCs, thermoelectric generators are another kind of effective energy harvesting devices to generate electricity but from heat, which promises for applications in solar thermal utilization and waste heat recovery. However, conventional thermoelectric generators are constructed by inorganic materials, which are rigid and suffer a complicated fabrication. CPs may provide a potential solution for boosting the development of thermoelectric generators with high flexibility.[90] Meanwhile, they are lightweight and low-cost and readily scaled up through roll-to-roll printing technologies.

2.2.1. Working Mechanism

A representative structure of the flexible thermoelectric generator is shown in Figure 8, in which the n-type and p-type materials are connected by electrodes.[91] When a temperature difference is applied between the two electrodes of thermoelectric generator, the charge carriers including electrons and holes would transfer at the junction interface due to the different carrier concentrations, generating a potential that prevents the further diffusion by a drift current. As a result, a balance is reached between the diffusion and drift currents with the formation of an electric field, the intensity of which is mainly determined by the temperature. Typically, thermoelectric phenomenon is composed of three kinds of effects, i.e., Peltier effect, Seebeck effect and Thomson effect. For achieving high-performance thermoelectric...
generators, electrical conductivity and Seebeck coefficient should be enhanced while the thermal conductivity remains unchanged. However, a higher electrical conductivity will result in a lower Seebeck coefficient, and thereby a balance should be reached between the two factors. CPs such as PANI, PEDOT, PA, and PPy can also be utilized in thermoelectric generators.\textsuperscript{[92,93]}

2.2.2. Conjugated Polymer as Electrode Material

The CPs used in thermoelectric generators were usually prepared by electrochemical polymerization due to the uniform nanoscale morphology and easily tunable doping level by varying the voltage.\textsuperscript{[96]} Post-treatments can further enhance the electrical conductivity of CPs by tuning the doping level. For example, a PEDOT:PSS film was subjected to ethylene glycol or formic acid, the PSS on the surface can be selectively removed, resulting in the decrease in doping level.\textsuperscript{[97]} Moreover, the PSS concentration and the oxidation level on the surface of the PEDOT:PSS film can be accurately controlled by doping with DMSO/$p$-toluenesulfonic acid monohydrate and dedoping with hydrazine/DMSO. The former increased the electrical conductivity of PEDOT and the latter selectively removed the insulating barrier of PSS and controlled the oxidation level of PEDOT.\textsuperscript{[98]} Additionally, PEDOT:PSS mixed with CNT exhibited an increase in the thermoelectric power factors, which were orders of magnitude higher than those of typical CPs due to the increase of conductivity.\textsuperscript{[99]}

3. Conjugated Polymer for Flexible Energy Storage

Energy harvesting and storage will keep attracting increasing attentions owing to the energy crisis throughout the world. The
flexible energy harvesting devices such as PSCs and thermoelectric generators based on CPs have experienced a tremendous development in the past decades, which raises higher standard for the flexible energy storage devices, such as high energy capability, and good flexibility. The commonly used commercial energy storage devices mainly contain supercapacitors and LIBs. Supercapacitors as one of extraordinarily promising prospects for energy storage devices possess many unique advantages, such as easy fabrication, higher energy density than that of traditional electrical double layer capacitors (EDLCs), higher power density capable of fast charging/discharging compared to that of commercial LIBs and high cyclic stability. In contrast, LIBs exhibit higher energy densities than those of supercapacitors. Therefore, supercapacitors and LIBs are usually used for different practical applications.

However, the abovementioned two devices are generally appearing as rigid and bulk configuration, where the inorganic materials are widely applied, e.g., carbon nanomaterials, metal oxides, and metal alloys. Traditional inorganic materials show high energy storage performances, but make it difficult to realize the flexibility of energy storage devices with low cost for large-scale productions. CPs are the promising candidates for flexible energy storage devices due to their high electrical conductivity, large energy capability, and low cost. More importantly, they can enable energy storage devices to be flexible to meet the requirements for applications in electronic skin and portable equipment. Here we primarily focus on the recent applications of CPs in flexible supercapacitors and LIBs.

3.1. Supercapacitor

Typically, the flexible supercapacitor is constructed by sandwiching the gel electrolyte between two flexible electrode materials. The substrates such as poly(ethylene terephthalate), poly(dimethylsiloxane), textile and cloth, and gel electrolyte are all highly flexible, and thereby we mainly highlight the recent progress of flexible electrode materials based on CPs in flexible supercapacitors.

3.1.1. Working Mechanism

Supercapacitors are well accepted to classify into EDLCs and pseudocapacitors. For EDLCs, the charge storage process is conducted by reversible ion adsorption between the surface of electrolyte and electrode to form a double layer structure. The capacitance originates from the electrostatic charge accumulated at the electrode/electrolyte interface. Carbon nanomaterials including ordered mesoporous carbon, activated carbon, carbide-derived carbon, CNT, and graphene have been widely explored as electrode materials for EDLCs. ELDCs can provide high power density coupled with stable charge/discharge cyclic performance but they suffer from low energy density because of their working mechanism. Subsequently, the pseudocapacitive materials were introduced to form pseudocapacitors to significantly enhance the energy density due to their fast and reversible surface redox reactions at the electrolyte/electrode surface.\[100\] The commonly applied pseudocapacitive materials include metal oxides (RuO$_2$, Fe$_3$O$_4$, V$_2$O$_5$, and MnO$_2$) and CPs, which reveal a much higher capacitance than that of materials for EDLC.

3.1.2. Conjugated Polymer as Electrode Material

CPs with high specific capacitance and high flexibility make a promise for constructing flexible pseudocapacitors. However, their electrical conductivity is not high enough, which makes it difficult to reach the standard of high power density required by supercapacitors, especially at high current densities. Great efforts have been made to solve this problem, and one of the most effective approaches is introducing the highly conductive materials such as carbon nanomaterials into the CPs. After compositing, the rate capability and cyclic stability of supercapacitor are improved dramatically without sacrificing the flexibility. Here the carbon nanomaterial cannot benefit for the enhancement of specific capacitance. Furthermore, higher capacitive materials such as transition metal oxides/hydroxides are also introduced to obtain the multielement composites, which can reach a higher energy density for the flexible electrodes.

Pure Conjugated Polymer: CPs including PANI, PPy, and PEDOT are typically used in supercapacitors for their many desirable properties such as a combined high specific...
capacitance, electroactivity, and doping level.\textsuperscript{[101–103]} As a demonstration, the doping mechanism of PANI is shown in Figure 9a.\textsuperscript{[100]} PANI is protonated through a redox reaction which involves the conversion from its semiconductor (emeraldine base) to metal (emeraldine salt) state, resulting in a structural change in the unpaired spin per repeat unit with a positive charge.

A typical PANI electrode is shown in Figure 9b,c, which possesses an excellent flexibility.\textsuperscript{[101]} With further enhancing the specific area surface, a flexible supercapacitor based on PANI nanowire arrays is reported with a high capacitance of 588 F cm\textsuperscript{−3} and high rate capability.\textsuperscript{[104]} The cyclic stability was further enhanced by designing a crosslinked structure into PANI through the use of hydrothermal method.\textsuperscript{[105]} This was mainly ascribed to the stable net structure in PANI backbone, which can well accommodate mechanical strain during cycling.

PPy offered a greater degree of flexibility in electrochemical processing than most CPs.\textsuperscript{[106–110]} PPy nanorods can be directly deposited onto soft cotton fabrics to construct flexible supercapacitors with a high specific capacitance of 325 F g\textsuperscript{−1} and an energy density of 24.7 Wh kg\textsuperscript{−1}.\textsuperscript{[106,107]} However, the cyclic stability of supercapacitor needed to be improved for practical applications. Through the design of a hollow capsular structure for PPy, the stability can be enhanced with the specific capacitance being maintained by above 90% after 11 000 charge/discharge cycles.\textsuperscript{[111]} Such a high stability came from the unique tubular structure of PPy that has porous capsular walls. The voids in the hollow fibers and among the capsules offer enough space to accommodate volume change during the doping/dedoping process. The advances on PEDOT have also grown rapidly due to its wide potential window originated from the electron-rich structure.\textsuperscript{[112]}

Figure 9. The working mechanism and morphology of PANI in supercapacitor. a) Schematic illustration of the doping mechanism of PANI. Reproduced with permission.\textsuperscript{[100]} Copyright 2001, American Physical Society. b,c) Schematic of the structure and photograph of the flexible PANI electrode. Reproduced with permission.\textsuperscript{[101]} Copyright 2014, Springer.
Composite: Pure CP electrodes typically suffer from poor cyclic stability owing to the generation of rupture caused by the large volume variation between the doped/dedoped states during the charge/discharge process. Carbon materials are attractive due to their low cost, good chemical and thermal stability, and high electrical conductivity and mechanical properties. Therefore, compositing CPs with carbon materials is effective to improve the stability of CPs. In the past decades, there have been many reports on the composites of CPs and carbon nanomaterials.

CNT and graphene as two standard materials are widely used to form composites with CPs for flexible supercapacitors due to their high chemical and electrochemical stability, large surface area, and high electrical conductivity.\(^{[113–121]}\) PANI nanorods were directly coated onto the high-quality graphene paper\(^{[122,123]}\) or woven fabric\(^{[124]}\) to construct freestanding and flexible PANI nanorod/graphene composites for supercapacitors. The PANI/graphene paper based supercapacitor exhibited higher specific capacitance and better cyclic stability than that of the pure graphene or PANI due to a synergistic effect of graphene and PANI, the specific capacitance of which preserved 96% after 1000 cycles.\(^{[122–129]}\)

However, the specific surface area of electrode was relatively low, which limited the performances. In order to enhance the specific area, one effective solution is introducing a porous structure\(^{[130]}\) or interconnected network, e.g., carbon cloth. For example, CPs can be coated onto a flexible carbon cloth by an interfacial polymerization method.\(^{[126,131]}\) As the overall supercapacitor was fabricated on the cloth, the mechanical flexibility was enhanced dramatically. Furthermore, reduced graphene oxide (rGO) was introduced into this system to enhance the contact between CP and carbon cloth so as to increase the electrical conductivity, resulting in a high specific capacitance of 1145 F g\(^{-1}\).\(^{[132]}\) CPs can also act as barriers to prevent the loss of the inner electroactive material, thus improving the cyclic stability. For example, a bilayered polymeric composite of poly-2,5-dimercapto-1,3,4-thiadiazole and PPy was continuously electrodeposited onto the carbon fiber cloth as electrodes for supercapacitors with the specific capacitance of nearly 1130 F g\(^{-1}\) after 100 cycles.\(^{[133]}\)

Apart from the direct coating on the carbon-based substrate, the carbon nanomaterials, e.g., graphene oxide (GO), can be premixed with PEDOT:PSS to form a mixed solution, and it was then bar-coated on a flexible hydrophilic polyvinylidene fluoride membrane substrate to form an electrode for supercapacitor with a maximal areal specific capacitance (448 mF cm\(^{-2}\)) (Figure 10).\(^{[134]}\) However, by this method, the GO materials were usually agglomerated, which was harmful to the electrochemical performance. To avoid this problem, a novel PPy/graphene intercalation structure was designed to prevent restacking of the graphene sheets, resulting in a large electrolyte/electrode interface for charge storage and ion transport.\(^{[135]}\) The graphene sheet accommodated the volume change within PPy to prevent a loss in capacitance during repeated doping/dedoping processes. Due to the synergistic effect arising from two components, the resulting supercapacitor exhibited a high flexibility.

The supercapacitors based on the combination of carbon materials and CPs exhibited improved specific capacitances and power densities besides the flexibility. However, the performance is still far from the expectation for practical applications. Recently, the use of transition metal oxides/hydroxides such as MnO\(_2\), RuO\(_2\), CoO/Co\(_2\)O\(_4\), NiO/Ni(OH)\(_2\), Co(OH)\(_2\), and Fe\(_2\)O\(_3\) has been studied as an effective strategy for high-performance supercapacitors based on their high specific capacitances, although the electrical conductivity is relatively low.\(^{[136–142]}\) To this end, metal oxides were introduced to the composite with a high specific capacitance of 2244 F g\(^{-1}\) by coating highly ordered 3D PPy/NiCo\(_2\)O\(_4\) nanowires on carbon textiles.\(^{[13]}\) The introduced hydrous RuO\(_2\) nanoparticles attached to the PEDOT:PSS/graphene surfaces allowed for redox reactions with the surrounding electrolyte so as to increase the specific capacitance of the electrode materials (Figure 11).\(^{[143]}\) CPs can effectively improve the electrical conductivity of transition metal oxides/hydroxides. PPy was used to accelerate the electron transfer of metal oxides, and the supercapacitor with the structure of NiCo\(_2\)O\(_4\)/PPy core–shell nanowires coated on carbon microfibers exhibited high pseudocapacitive performance of 2055 F g\(^{-1}\).\(^{[144]}\)

PANI was also employed to enhance electrical conductivity of cobalt-based metal–organic framework (MOF) crystals and Faradic processes at the interface by electrochemical deposition (Figure 12).\(^{[145]}\) Here, PANI was not only deposited on the surface.
of MOFs but also a bridge to interconnect isolated MOF particles by covering the interparticle open space. Moreover, the embedding of interconnected PANI nanorods into interlaced MnO2 nanoflakes can also enhance the contact area between the electrode and electrolyte to benefit the fast ion diffusion (Figure 13), which enabled charge transfer and ion transport.\[146\]

After compositing, the stability of supercapacitors was also remarkably improved. The specific capacitance was maintained by 90% after charging/discharging for 5000 cycles by using ZnCo2O4/PPy/Ni hybrid electrodes. Such a high stability was mainly attributed to high electrical conductivity rendered by the integration of PPy and short ion diffusion pathways from the porous structure of PPy nanofilms and ZnCo2O4 nanowires.\[147\]

PANI/C/TiN nanowire array with a coaxial shell/shell/core structure was prepared by continuously coating carbon and PANI on TiN nanowire array for supercapacitors with a high specific capacitance of 1093 F g\(^{-1}\) at 1.0 A g\(^{-1}\) and a good capacity retention by 98% after 2000 cycles. The electroactive PANI shell can enable a reversible doping/dedoping reaction to enhance pseudocapacitance. The carbon shell was used to protect TiN from the electrochemical corrosion so as to enhance the cyclic stability. The TiN core nanowire array provided an effective electron transfer route. This coaxial PANI/C/TiN nanowire array offered the ion diffusion channel within the neighboring nanowires and the electron transport route along nanowires, which promised for supercapacitors with high performances including a high flexibility.\[148\]

The flexibility can be further enhanced by designing the supercapacitors in a fiber format with MnO2/PPy/carbon and V2O5/PANI/carbon fiber composites as two electrodes.\[149\] This fiber-shaped supercapacitor can be bent or twisted repeatedly without any obvious damage. The characterization on the flexibility of the supercapacitors is similar to that of PSCs mentioned above, i.e., tracing the variation of the specific capacitance of the supercapacitors under repeated bending. Moreover, these fiber-shaped supercapacitors can also be designed with many new functions, such as stretchability\[150\] or color change with the different voltages,\[31\] to satisfy various requirements. As shown in Figure 14, the fiber-shaped supercapacitor based on CNT sheet/PANI electrode was developed with specific capacitance to be maintained by 93.8% after bending for 1000 cycles and 97.9% after stretching for 100 cycles at a strain of 100%. The smart supercapacitor can exhibit different colors with the voltage changed during the charge/discharge process because of the unique electronic property of PANI, which dramatically extended the application area for supercapacitors. As expected, the flexible powering textiles can be achieved by weaving them together to drive commercial light-emitting diodes.\[151,152\] The electrochemical performances were well maintained during bending, indicating a stable electrochemical property. The
Figure 12. Flexible supercapacitors based on the PANI/MOF/carbon cloth electrode. a) Schematic illustration showing that electrons cannot migrate or access the skeleton of MOF crystals, while the electrolyte can move in and out of the MOF pores by diffusion effect. b) Schematic illustration indicating that, after depositing with PANI, both electron and electrolyte can access MOF crystals. c) Schematic illustrations and SEM images during the preparation of PANI/MOF/carbon cloth electrode. Reproduced with permission.[145] Copyright 2015, American Chemical Society.

Figure 13. Schematic illustration of the fabrication preparation of rGO/MnO$_2$/PANI nanocomposite. Reproduced with permission.[146] Copyright 2015, The Royal Society of Chemistry.
comparison of specific capacitance and stability in abovementioned supercapacitors is made at Table 3.\textsuperscript{95,100,122,132,137,138}

3.2. Lithium-Ion Batteries

LIBs are widely investigated for high energy density, long-term stability, and low charge loss. The realization of flexibility may greatly promote their applications in many emerging fields such as electronic skins and sensors.

3.2.1. Working Mechanism

A typical LIB is composed of cathode and anode electrodes, separator and electrolyte. The working mechanism is based on the reversible intercalation and deintercalation processes of Li\textsuperscript{+} ions in the active materials of electrodes.\textsuperscript{153} During charging, Li\textsuperscript{+} ions are removed from the cathode, transferred to the electrolyte, and intercalated into the anode. Meanwhile, the current flows from the anode to the cathode at the external circuit.

3.2.2. Conjugated Polymer as Electrode Material

Currently, CPs have also been explored as active materials of electrodes for flexible LIBs.\textsuperscript{154-156} However, their resultant capacities were much lower than those of conventional electrode materials. Meanwhile, the poor cyclic stability significantly prevented CPs from applications in LIBs, mainly due to the structural units inactive caused by the irreversible overoxidation reaction at the high voltage during the charge/discharge process.
An effective strategy to solve this urgent problem is combining CPs with inorganic materials to construct flexible composite electrodes for LIBs (Figure 15). Because CPs can interact with inorganic compounds synergistically, remarkable improvements in rate capabilities, electrode lifetime and mechanical and thermal stability have been achieved. The LIB with the PPy/LiFePO_4 composite electrode exhibited a higher discharge capacity beyond 50 cycles (80 mA h g\(^{-1}\)) than that of an LIB with pure LiFePO_4 (60 mA h g\(^{-1}\)) by enhancing the electrical conductivity of the electrode. Although the current performance of flexible LIBs based on CPs is limited and can be greatly increased, the development of flexible LIBs will be boosted with the appearance of new CPs with high performances.

Note that, a new type of well-studied nonconductive polymers, polyimide derivatives, has emerged as electrode materials for LIBs considering their high mechanical strength, thermal stability, nonflammability, scalable preparation, and low cost. They can be reduced and oxidized, compensating with the association and disassociation of Li\(^+\) ions with oxygen. The resulting cathode exhibits higher working voltage, capacity, and energy density than previously reported organic cathode materials, which promises a fertile research area.

Because most polymer-based electronic devices are sensitive to air and water, the barriers are critical for achieving highly stable flexible energy devices. Common polymer barriers contain thermoplastic semicrystalline polymers (e.g., poly(ethylene terephthalate)), thermoplastic noncrystalline polymers (e.g., polycarbonate), and high-Tg materials (e.g., polyimide), which should possess many excellent properties such as sealability, thermal conductivity and electrical insulation.

### 4. Conclusion and Perspective

Here, the recent advances in flexible energy harvesting and storage devices based on CPs are highlighted. The CP dramatically extends the applications of energy devices by enabling them to be compatible with flexible and nonplanar substrates so as to promise for many new emerging and encouraging applications such as electronics, aerospace, transport, and biomedical field. A novel structure by designing them into a fiber shape is also discussed, which can better adapt to the 3D deformation. A wide variety of CPs forms composites with highly conductive and capacitive materials including carbon nanomaterials and metal oxides, and they have been employed as electrodes or active components to construct flexible energy harvesting and storage devices with better performances. Up to now, the flexible PSC has achieved a high PCE of nearly 9.4%, while the specific capacitance of the flexible supercapacitor exceeds 2000 F g\(^{-1}\). However, there still exists much room for further enhancement in performance, stability, and flexibility.

For the CPs used in energy harvesting devices, in particular PSCs, they should possess the suitable energy level and excellent electronic properties for effective charge separation and transport. Meanwhile, the donor and acceptor materials should build a suitable bandgap to enlarge the solar spectrum coverage. A much deeper mechanism understanding of the electronic interaction involved in the entire devices should be focused on and the updated new materials must be correspondingly designed in combination with this new understanding. Great efforts should also be made to develop new CP-based acceptor materials as well as electron-transporting materials that are critically important for the realization of fully flexible PSCs. Moreover importantly, the CP-based acceptor materials with the suitable tunable energy level can rapidly break through the efficiency bottleneck of current PSCs. For practical applications, the stability of PSCs should also be addressed. On the one hand, the replacement of conventional hole-transporting materials, e.g., PEDOT:PSS, with new materials is critically important because of its water absorption. On the other hand, a concept of the inverted structure indicates an exciting approach to improve the stability of PSCs without the use of the corrosive and hygroscopic PEDOT:PSS and low-work-function cathode that are harmful to device lifetime.

In addition, for flexible electrochemical storage devices, CPs are promising candidates for electrode materials owing to their high specific capacitances and good flexibility. However, a major challenge for CP-based electrodes is a low cyclic stability, which is mainly attributed to the volume change of electrodes upon doping/dedoping during the charge/discharge process. An effective strategy for solving this problem is introducing a porous structure to the CPs, which can greatly enhance the cyclic stability by adapting to the volume changes during the doping/dedoping process coupled with the increase in specific surface area for fast and effective charge transfer. Moreover, CPs can be further composited with highly conductive carbon nanomaterials as well as high-capacitive metal oxides for further enhancement of the electrochemical performance through a synergistic effect.

To conclude, the relatively low device efficiency and stability have remarkably limited the further advance of the flexible
energy harvesting and storage devices. Additionally, the next-generation flexible electronic devices require the integration of more functions such as sensing and shape memory besides energy harvesting or storage to better meet the requirements in practical applications. Therefore, more efforts should be made to design new and promising CPs with much increased electronic and mechanical properties for much higher performances mentioned above. These flexible energy devices open up a new direction in the multidisciplinary fields across chemistry, physics, biology, and engineering. They are promising for a wide variety of emerging application areas such as portable and wearable electronics, and may change our life in the near future.

Acknowledgements
This work was supported by MOST (2016YFA0203302), NSFC (21634003, 51573027, 51403038, 51673043, 21604012), and STCSM (16JC140072, 15XD1500400, 15JC1400200).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
conjugated polymers, flexible, lithium-ion batteries, polymer solar cells, supercapacitors

Received: July 29, 2017
Revised: November 1, 2017
Published online: February 5, 2018
