

Biodegradable Materials and Green Processing for Green Electronics

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There is little question that the “electronic revolution” of the 20th century has impacted almost every aspect of human life. However, the emergence of solid-state electronics as a ubiquitous feature of an advanced modern society is posing new challenges such as the management of electronic waste (e-waste) that will remain through the 21st century. In addition to developing strategies to manage such e-waste, further challenges can be identified concerning the conservation and recycling of scarce elements, reducing the use of toxic materials and solvents in electronics processing, and lowering energy usage during fabrication methods. In response to these issues, the construction of electronic devices from renewable or biodegradable materials that decompose to harmless by-products is becoming a topic of great interest. Such “green” electronic devices need to be fabricated on industrial scale through low-energy and low-cost methods that involve low/non-toxic functional materials or solvents. This review highlights recent advances in the development of biodegradable materials and processing strategies for electronics with an emphasis on areas where green electronic devices show the greatest promise, including solar cells, organic field-effect transistors, light-emitting diodes, and other electronic devices.

industry. With the adoption of Moore's Law as a driving force for progress, electronics technology has grown at an exponential rate. In turn, the regular availability of increasingly powerful and/or cheaper computer chips has seen the global adoption of electronics technology in ever-increasing complex arrays of consumer, industrial, medical, space, and military applications. The economic and societal benefits of modern electronics cannot be underestimated, with almost every aspect of modern human endeavor influenced, on some level, by solid-state electronic devices. Statistically, the global consumer electronics market was valued at approximately 1172 billion USD in 2017, and it is expected to reach approximately 1787 billion USD in 2024.^[1] When the sheer volume of electronic equipment and corresponding semiconductor devices such as silicon solar cells is combined with rapid turnover as older technology is superseded in a relatively short timeframe,

a significant volume of electronic waste (e-waste) is created. For example, it has been estimated that 20–50 million ton of consumer electronic products are discarded globally every year.^[2] This represents approximately 5% of the current municipal solid waste worldwide. Compounding the escalating volume of e-waste from consumer electronics, the global distribution of other semiconductor-based devices, such as rooftop photovoltaic cells, is rapidly growing. Although the lifetime of such

1. Introduction

The development of the integrated circuit in 1959, largely credited to the work of Jack Kilby (Texas Instruments Inc., Texas, USA) and Robert Noyce (Fairchild Semiconductor International, Inc., California, USA), has served as a prelude to the immense global scientific and engineering effort that has underpinned the growth of the modern solid-state electronic

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devices is significantly longer than consumer electronics, it has been estimated that there will be 35 000 ton of photovoltaic waste by 2020, growing to 60 million ton by 2050.^[3]

Unless steps are made to recover, recycle, and reduce our reliance on conventional solid-state electronic devices, this volume of e-waste will seriously and negatively impact the environment.^[4] Many semiconductor devices contain significant amounts of toxic elements, including mercury, arsenic, chromium, and lead (Pb), which can leach into soils and waterways when e-waste is disposed of in landfills; meanwhile the incineration of plastics leads to the release of volatile compounds such as dioxin derivatives, polychlorinated dibenzofuran, and polychlorinated biphenyls, which are known group 1 carcinogens.^[5,6]

The desire to reduce the volume and consequent impact of e-waste has brought about a growing interest in “green electronics,” whereby some functions and device structures that are currently associated with semiconductor electronics are replaced with devices containing more environmentally friendly materials. According to European Standard EN13432, at least 90% of all materials used in green electronics must be converted within 6 months of abandonment into harmless components, such as water, carbon dioxide, and biomass, through the action of fungi or microorganisms under certain defined conditions of temperature, humidity, and oxygen concentration.^[7,8]

In addition to eliminating (or at least reducing) the use of toxic materials in the processing methods and final products of green electronic technologies, the use of degradable materials offers additional, if perhaps niche, advantages for several different applications. Insecure disposal of e-waste may permit the recovery and exploitation of confidential data by others. The automatic degradation of materials used in green electronics ensures that any data previously stored will become permanently corrupted, thereby guaranteeing security.^[9] The use of biodegradable or biocompatible materials within the context of green electronics may also be advantageous in the development of medical implants by limiting the need to surgically remove devices post-diagnosis, monitoring, or therapy, thereby improving patient outcomes.^[10] Furthermore, the advent of wearable electronics is also gaining interest in regard to biocompatible and biodegradable electronic materials, particularly on flexible substrates.^[11] This article sets out to review recent advances in the development of the materials and processing strategies that underpin the development of green electronics. These advances are exemplified through reference to areas where green devices show the greatest potential, and they include solar cells, organic field-effect transistors, light-emitting devices, and other electronic devices.

2. Biodegradable Materials and Devices

2.1. Overview of Biodegradable Materials

A working electronic device is considered to consist of several components including substrates, electrodes or interconnect materials, and active layer materials. This section provides an overview of the biodegradable materials that have been explored for use in these different components and a summary



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of the mechanisms by which these materials can be degraded. The use of these materials in the design and fabrication of biodegradable devices, including solar cells, organic field-effect transistors (OFETs), light-emitting diodes (LEDs), batteries, and biocompatible implantable devices for healthcare is discussed.

2.1.1. Biodegradable Substrates

A variety of rigid and flexible substrate materials have been developed for use in conventional solid-state and polymer electronics. The remarkable semiconducting properties of silicon/silicon dioxide (Si/SiO₂) substrates used in conventional solid-state electronics have driven the electronic revolution. The development of advanced nanofabrication techniques, doping strategies, and the manipulation of the crystal lattice in these Si substrates, coupled with the development of complementary solid-state materials, have permitted the relentless evolution of solid-state electronics. The development of conducting and semiconducting polymers has generated a considerable interest in lightweight, flexible, and even stretchable polymer or plastic substrates to fully utilize the roll-to-roll manufacturing process to accelerate the commercialization of larger but lighter weight electronic products, which holds particular promise for lighting and display applications. In regard to green electronic technologies, substrates must display a combination of electrical, physical, and mechanical properties appropriate for the desired applications but also be (bio)degradable to innocuous or recoverable constituents. To these ends, substrates based on natural paper fibers and a variety of synthetic polymers such as polydimethylsiloxane (PDMS), polyvinyl alcohol (PVA), and polylactic acid (PLA) have all been identified and explored.^[8]

Natural-Based Substrates: Paper is readily identified as a substrate for printed electronics given the advanced state of roll-to-roll printing methods.^[12] The high surface roughness of commercial papers that results from the porous structure of the paper fiber network could be advantages for energy storage devices where large surface area is important for easy absorption of electrolyte and binding with nanomaterials. Moreover, the incorporation of conductive materials (i.e., carbon nanotube (CNT), silver nanowire (AgNW), metal oxides, graphene, and conductive polymers) within the paper results in a sufficiently high electrical conductivity for the subsequent hybrid materials, which are then used as substrates in devices such as supercapacitors.^[13] Indeed, some devices prepared on such modified conducting paper substrates have performed comparably with analogous devices deposited on flat conducting polymer substrates.^[12,14] However, the porosity and high roughness of the paper could be detrimental to thin film devices, especially those utilizing organic materials as semiconducting or dielectric layer. This problem is usually remedied by coating or laminating with wax, kaolin, starch, latex, and polymers such as polyethylene, polypropylene, polyurethane, and PVA. So far, paper substrates have been used in various electronic devices including solar cells,^[15,16] organic LEDs (OLEDs),^[17,18] biobatteries,^[19] sensors,^[20,21] transistors,^[22] displays,^[23] and radio frequency identification devices.^[24]

To expand the range of potential applications for paper-based green electronics, Hu et al. have described a relatively simple

method for the preparation of transparent paper substrates directly from thin (400 μm to 1 mm) wood slices cut perpendicularly to the direction of growth.^[25] After removal of the lignin, the resulting loose array of lumen (tubular structures composed of cellulose microfibrils and nanofibrils) that was aligned parallel to the direction of growth was pressed along the lumen axis, causing the lumen to collapse in random directions. The resultant material was composed of an isotropic array of fibrils and had a dense layered structure with a low propensity to diffract light; a transmittance of approximately 90% was observed in the resulting "isotropic paper." A simple device constructed by contacting a graphene flake with two gold (Au) electrodes deposited through a shadow mask exhibited ohmic contact, while the introduction of a gate electrode and addition of an electrolyte exhibited a bipolar transistor response. This paper was readily degraded when returned to soil.

Another transparent substrate based on natural fibers is chitin (poly- β -(1,4)-N-acetyl-D-glucosamine) nanofiber-based transparent paper developed by Bae et al. and used as the substrate in an OLED device.^[18] Initially, hexafluoroisopropanol was used as the solvent to disrupt the intermolecular hydrogen (H)-bonds in the β -chitin. A 0.4% w/v solution was prepared in this way and concentrated to yield a 2.4% alcogel, which was then centrifugally cast to yield a chitin-based paper with virtually 100% transmission in the visible region after processing. Multi-layer OLED devices of the structure ZnS (25 nm)/Ag (7 nm)/MoO₃ (5 nm)/NPB (50 nm)/Alq₃ (50 nm)/LiQ (1 nm)/Al (100 nm) (ZnS: zinc sulfur; Ag: silver; MoO₃: molybdenum trioxide; NPB: N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine; Alq₃: tris(8-hydroxyquinolino)lithium) were fabricated on these transparent chitin papers and they performed similarly to devices fabricated on polyethylene naphthalate (PEN) plastic substrates, exhibiting a maximum luminance (L_{max}) of 3 890 cd m^{-2} .

Silk films and fibers are also suitable natural substances for the engineering of paper-like electronic substrates, as they exhibit biocompatibility and biodegradation rates that can be tuned from minutes to days through appropriate modification. Silks are readily available from a wide range of sources that are low in cost and easy to process. The combination of these features is inspiring further exploration of these materials for potential applications to electronics in the biomedical industry (i.e., food sensing applications,^[26] improvement of physiological recording and targeted drug delivery,^[27] and biomedical implants).^[28]

Fibroin, an insoluble protein present in the silks produced by a variety of moth genera and insects, offers several features that can be exploited in the production of paper-like substrates for green electronics; these features include excellent biocompatibility, slow degradation in vivo, ease of chemical modification, and processability from either aqueous solutions or organic solvents.^[29] Recently, Zhao et al. have demonstrated the use of paper-like fibroin films as the substrates for memory devices.^[30] These films can degrade within 24 h in a phosphate-buffered saline (PBS, pH = 7.4) solution. These fibroin substrate-based devices display excellent flexibility and switching performance, and the mechanical stresses and bending deformations of the devices have no obvious influence on the I - V characteristics of the high and low resistance states.

Other natural materials that are widely available and offer potential applications as biocompatible and biodegradable substrates include shellac, hard gelatine, collagen, chitosan, alginate, and dextran, among many others. For example, shellac is secreted by female lac beetles to form tunnel-like tubes as the beetles traverse tree branches, from where the shellac can then be harvested.^[31] After processing, shellac forms a film that is generally quite smooth, which is extremely helpful in electronic applications. Hard gelatine contains properties similar to shellac and can also form biocompatible films with smooth surfaces. Although the use of shellac and hard gelatine as substrates is still in its initial stages, Irimia-Vladu et al. have reported transistor devices with good electrical characteristics that have been fabricated from several different organic semiconducting materials supported by shellac and hard gelatine substrates.^[32] Although these natural-based substrate materials have the advantages of resource abundance, low cost, biodegradability, and negligible immunoreaction to human body, there are some limitations for their wide applications and performance improvement of fabricated devices. For example, good biodegradability indicates relatively low environmental stability. Consequently, certain conditions and processes used during device fabrication, such as high temperatures and harsh solvents, may not be compatible with the properties of natural product-based substrates. In addition, the variable degradation rates of different substrates would not match the requirements of certain long-life devices. All these drawbacks significantly influence the wide applications and limit the device performance improvement. Therefore, environmentally compatible synthetic substrates, the properties of which can be tuned through judicious choice of reactants, attract attention.

Synthetic-Based Substrates: A variety of synthetic polymers, known for their use in biomedical implants, have also been identified as potential materials to construct film-like substrates for green electronics.^[33] For example, PDMS has been approved for use by the National Heart, Lung, and Blood Institute of the United States, has proven to be an excellent substrate in flexible and stretchable electronics.^[34–36] The readily modified chemical structure of the polymer has allowed for a good degree of engineering of the resulting polymer properties,^[37] and various synthetic polymer-based devices have been fabricated and implanted into living tissues to study functions in both medical diagnosis and therapy.^[38] Other biodegradable and biocompatible synthetic polymers, including polycaprolactone (PCL), poly(3-hydroxybutyrate) (PHB), poly(4-hydroxybutyrate), poly 3-hydroxyoctanoate, poly(glycolic acid), poly(L-lactide), poly(glycolide-co-caprolactone), poly(lactide-co-ε-caprolactone), poly(glycerol sebacate) (PGS), and poly(1,8-octanediol-co-citrate), have been explored in similar applications. Specific details regarding electronic devices based on these biodegradable substrates will be discussed in Section 2.3.

2.1.2. Biodegradable Electrodes or Contact Materials

Metals or alloys are the first choice for electrodes or contact materials because of their high conductivity in electronic devices.^[39–41] There is a general notion that these types of materials are difficult to degrade and may injure the human body

if the resultant devices are used in the medical field. However, in electronics, the metal electrodes are ultra-thin films with limited capacity for harm. However, metals such as Au, Ag, platinum (Pt) and copper (Cu) may not be suitable for green electronics because of their non-biodegradable nature even in the state of an ultra-thin film. The commonly used metals as electrodes and contacts in green electronics are iron (Fe), magnesium (Mg), zinc (Zn), and their alloys and oxides.^[42] Such metal thin films are biocompatible with the human body and easy to dispose.^[10] Rogers et al. measured the dissolution rates of several metallic nanomembranes and found that although the dissolution rates are different, some metal thin films can be dissolved in deionized (DI) water and simulated body fluids (Hanks' balanced salt solution, HBSS). These metal thin films have also been used to construct short-life time devices, thereby demonstrating their feasibility as biodegradable electrodes for green electronics.^[43] Figure 1-i shows the dissolution behaviors of several metal or alloy contacts and associated changes in electrical resistance. Although the dissolution rates vary, the thin film contacts are all biodegradable in DI water or HBSS (with pH values of 5–8). Most metals can be dissolved in acidic solution (pH < 7), as in the digestive system, illustrating why these metal films are considered biocompatible.

In regard to biodegradable electrodes or contacts, the main issue of concern is whether the metals are toxic or radioactive, thereby resulting in damage to the human body. Bao et al. fabricated biodegradable transistors using Fe, rather than Au, for electrodes to make the resultant devices completely degradable.^[9] Devices based on Fe electrodes demonstrate a greater negative threshold voltage compared with that of devices based on Au. This is because of the mismatch of the work function of Fe with the highest occupied molecular orbital energy level of the semiconductor, and an excellent hole mobility value of $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ can be achieved. Au is an edible substance and will not damage the human body; however, it is not biodegradable owing to its insolubility in common acid or base solutions. Thus, whilst Au electrodes can be used to create biocompatible electronics, they are not biodegradable. In the biodegradable electronic devices fabricated by Bao et al., the Fe electrodes can rapidly degrade within 1 h in an acidic solution with a pH of 4.6.^[32]

Other metals have also been reported as biodegradable electrodes for electronic devices with traceless dissolution in certain solutions. Mg is the most used metal electrode because it can dissolve in DI water, as well as acid and base solutions. Rogers et al. reported transient electronics where Mg/MgO is used as the electrode, along with other biodegradable materials such as Si/SiO₂.^[44] The device degrades in approximately 10 min after being dipped into DI water. They proposed the following mechanism (Figure 1-ii). When Si or Mg reacts with water, soluble Si(OH)₄ or Mg(OH)₂ is directly formed through hydrolysis. Sometimes SiO₂ or MgO can be formed as an intermediate that reacts again with water to form Si(OH)₄ or Mg(OH)₂. Besides dissolution in DI water and a well-known reaction with an acid to form soluble metal salt substances, Rogers et al. and Zhao et al. also studied the degradation of Mg in a base solution. Rogers et al. simulated body fluid using a PBS solution (pH = 7.4) at 37 °C, and the Mg electrode dissolved within 2 min.^[44] Zhao et al. used the same solution but increased the pH value to 10; it took the Mg electrode 12 h to

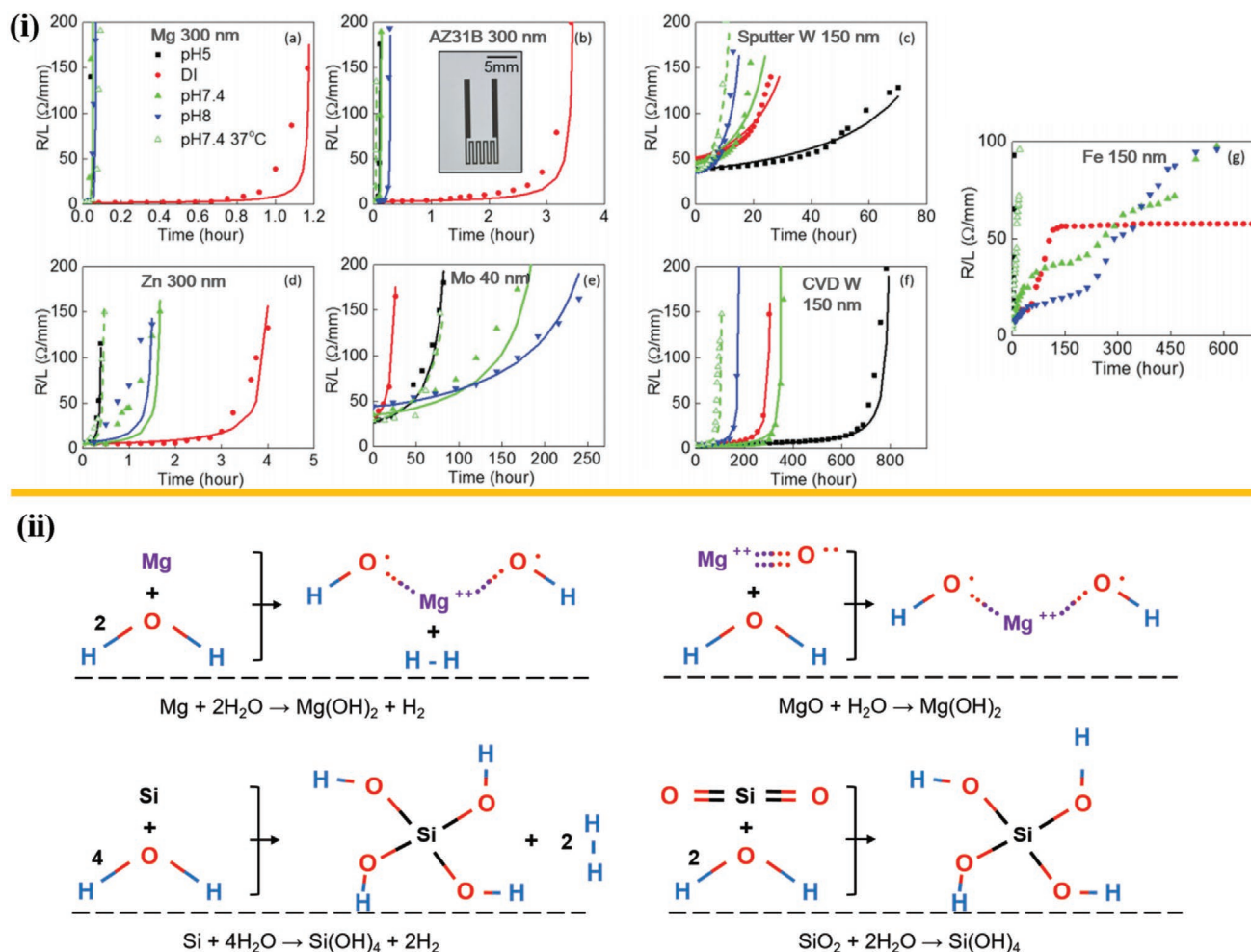


Figure 1. i) Dissolution behavior of metal or alloy thin film contacts in DI water and HBSS (pH = 5–8). Reproduced with permission.^[43] Copyright 2014, Wiley-VCH. ii) Proposed mechanism of Mg/MgO and Si/SiO₂ chemical reaction in DI water. Reproduced with permission.^[44] Copyright 2012, American Association for the Advancement of Science.

dissolve at room temperature (25 °C), which was significantly longer than it took at 37 °C, indicating that dissolution kinetics are highly dependent upon pH value and temperature.^[30] Many similar metal electrodes have been used in green electronics, such as Zn, tungsten (W), Fe, molybdenum (Mo), and their respective oxides, and they can be found within the published review papers cited in refs. [10,40,41].

Researchers have made significant attempts to develop certain organic materials into interconnects or electrodes. Several common high-conducting polymers including polypyrrole (PPy), polyaniline (PANI), polythiophene (PT), and PT derivatives, such as poly(3,4-ethylenedioxythiophene) (PEDOT), have been utilized successfully as electrode materials.^[10] These polymers have typically needed to be doped to achieve higher conductivity exhibited by similar metals (with conductivity of 10^1 – 10^5 S cm⁻¹); then, their conducting state could be used for the purpose of interconnects or electrodes. As reviewed by Prof. Alan G. MacDiarmid,^[45] the conductivity of conducting polymers can reach a similar value as those metallic conductors such as Ag and Cu. That is the reason why these conducting polymers are termed “synthetic metals.” As a representative sample, PEDOT:polystyrene sulfonate (PSS) has been widely

used as the electrode material in organic electronics because of its ultrahigh conductivity. For example, Bao et al. reported a large-scale PEDOT:PSS film formed via solution shearing with a conductivity of 4600 S cm⁻¹. The organic photovoltaic (OPV) devices fabricated with this film as the electrode exhibited a comparable efficiency with that fabricated with indium tin oxide (ITO) electrode.^[46] Hori et al. reported the fabrication of an organic electronic device to deliver neurotransmitters in vitro and in vivo.^[47] In such a device, Hori et al. used PEDOT:PSS as both the anode and cathode electrodes because of its biocompatible property. When the device was connected to a circuit with an applied voltage, oxidation and reduction occurred repeatedly on the anode and cathode electrodes, respectively, and conductivity was achieved.^[47] With regard to the degradation of such conducting polymers, one strategy is to develop composite containing conducting polymers and biodegradable insulating matrix. In this case, the biodegradation is classified as type I (see Section 2.2) in which the matrix is degraded in suitable conditions and the non-degradable components are biocompatible. PEDOT:PSS, because of its biocompatibility, is thus used to develop conducting composite, belonging to this type. Another strategy to develop biodegradable conducting

polymers is to incorporate flexible and nonconjugated segments into the backbone structure. After degradation, the resultant small conjugated segments are not toxic and can be further degraded or removed by the environment or the body's immune system. This degradation is classified as type II (see Section 2.2). Some conducting polymers containing biodegradable segments in the backbone belong to this type, for example, polyurethane (DCPU).

Another representative organic electrode is the carbon nanotube (CNT) because of its metallic, semiconducting, and superconducting electron transport.^[48] CNT electrodes are widely applied in electrochemical devices^[49] because of their distinct properties that include nano-sized diameters, excellent electrochemical activities, electrical conductivity, and biocompatibility. Individual CNT electrodes offer remarkably high mass transfer coefficients because of the radial diffusion processes.^[50] These features greatly promote application in the electrochemical area.^[51,52] In addition, some modifications can be done with CNT^[53,54] that is incorporated with metal oxide, DNA, or graphene for a unique application in the subsequent devices. Despite these promising properties, it is still difficult to widely use organic materials as electrodes. For example, the use of orthogonal solvents for polymer electrodes (to ensure no damage occurs to the active layer materials) is a challenge in and of itself and complicates the fabrication of devices even more. The nano-sized CNT is often toxic; thus, the physiological efficacy cannot be confirmed. Additionally, individual CNT electrodes show vanishingly small response currents. Therefore, metals remain the preference for acting as electrode materials in green electronics.

2.1.3. Active Layer Materials

The development of green active layer materials poses the main issue that must be overcome for future commercialization of green electronic devices. The discovery of conducting organic polymers is particularly relevant to both the active layer in electronics and allied fields such as organic solar cells.^[55] Although some studies have classified dielectric materials (mainly available for OFETs and circuit design) to the active layer,^[8] in this review, we focused primarily on the conductors and/or semiconductors that are crucial for all types of electronic devices.

Because of their excellent conducting properties, traditional semiconductors are mainly based on metal oxides and Si derivatives (e.g., different forms of Si and Si germanium (Ge) alloys). A traditional device has typically been fabricated on a thick wafer. Because the resulting integrated circuit would not decompose for several hundred years, they are considered non-biodegradable. To facilitate the dissolution process for these types of materials, nanomembranes or nanowires were developed to improve their biodegradability. For example, Rogers et al. studied the transient form of Si by using a Si nanomembrane as the semiconductor to fabricate a series of workable devices, including resistors, photodetectors, field-effect transistors, and diodes.^[56] Great efforts have been devoted to investigating the dissolution mechanism of these types of materials in various biofluids and aqueous solutions. Most work has been focused on studying Si-based materials because of their excellent

operational characteristics and developed machining process. Conditions including pH values, temperatures, doping levels, and concentrations of certain elements, such as chlorides, phosphates, and calcium, have been studied.^[10] Some studies have shown that the nanomembranes could be fully decomposed within 10 days without generating toxic by-products.

Other than the aforementioned Si materials, there are other conductors that may serve as active layer materials, including metal oxides (e.g., gallium oxide, tin oxide [SnO₂], and indium oxide) and ternary oxides (e.g., ITO and fluorine-doped tin oxides [FTO]); these conductors, especially ITO, are widely used in solar cell applications without sacrificing the transparency of the resulting devices.^[57] Another representative material is zinc oxide (ZnO) because of its facile synthesis, high thermal stability, solution processability, and decent charge transport properties.^[58] Furthermore, the by-product of zinc hydroxide is a metabolite that can be processed by the human body. The degradation mechanisms of these materials can be confirmed through knowledge of dissolution chemistry, density functional theory, and molecular dynamics simulation tools. These efforts are helpful in designing materials to reduce the large quantities of future e-waste through detailed understanding of the break-down mechanisms. While traditional semiconductors have their own advantages, the emergence of conductive polymers is allowing researchers to focus on organic electronic devices and their intrinsic properties, which include the ease of structural modification, versatility for various electronic devices, solution processability, and the potential for large-scale production and low-cost products through the utilization of roll-to-roll technology.^[59]

The key for conductive polymers has been their conjugated structure that contains, in a broad sense, alternating single and double bonds along the polymer mainchain. In the beginning, the conductive synthetic polymers primarily included PPV, poly-phenylene vinylene (PPV), PANI, PEDOT, and PT (see their chemical structures in Figure 2). Now, the organic semiconductors have extended to a series of other materials which have excellent π -conjugation structure. The previous decades witnessed the tremendous advancement of organic semiconductors in organic, flexible, and printed electronics. Some of the π -conjugated motifs used as building blocks in organic semiconductors have developed into their own subjects of investigation; these included diketopyrrolopyrrole (DPP),^[60,61] isoindigo,^[62] naphthalenediimide (NDI),^[63] perylene diimide (PDI),^[64] benzothiadiazole (BT),^[65] benzodithiophene,^[66] carbazole,^[67] and triphenylamine (TPA).^[68] However, not all these materials have been proven suitable in green electronics because their C-C bonds usually resist to biodegradation. To overcome this issue, one effective strategy developed involved mixing non-biodegradable polymers with biodegradable, yet insulating, polymers. The resulting composites undergo type I degradation (vide infra), whereby the organic polymers were not disintegrated, but the biodegradable materials could be fully degraded.^[69] However, this strategy has not yet matured to the point of being ready for applications in green electronics.

Researchers have also tried to find naturally existing conjugated materials to construct semiconductors for electronic devices. Furan has shown the promise as a building block, as its derivatives are affordable from natural sources,^[70] and the

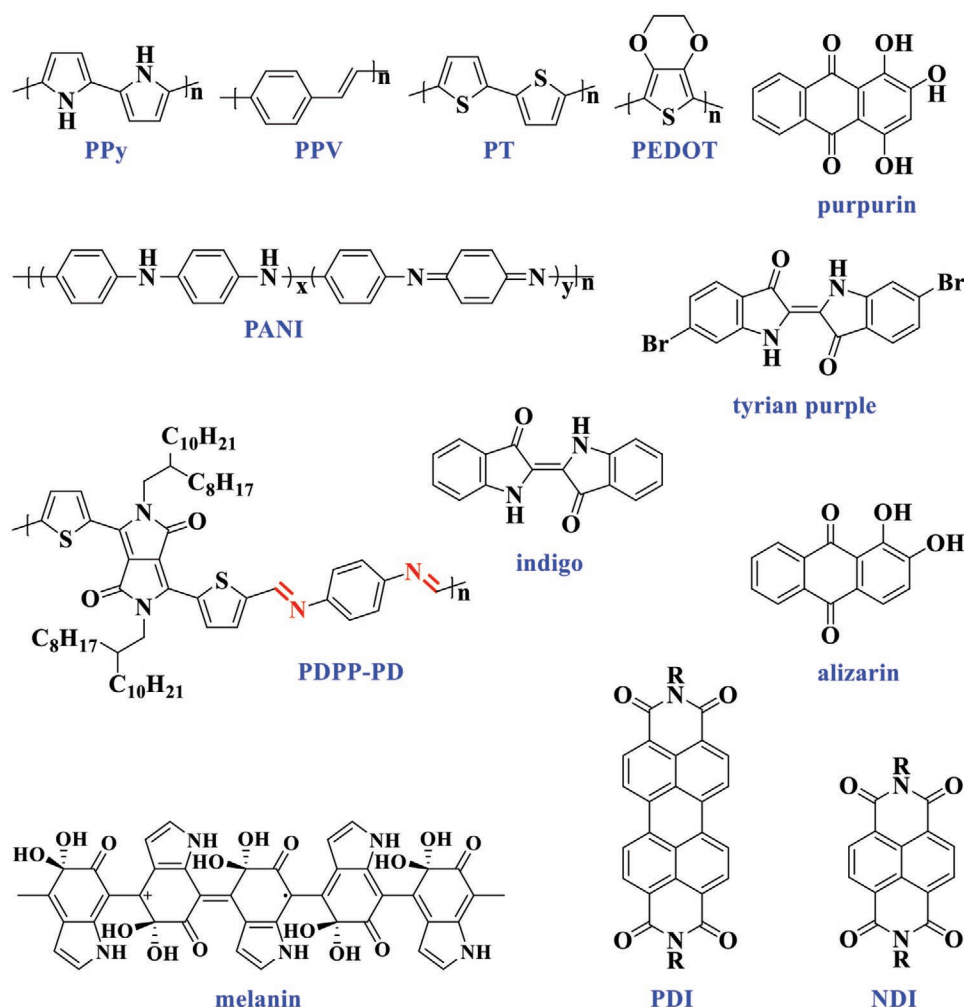


Figure 2. Chemical structures of various active layer materials (PPy: polypyrrole; PPV: poly-phenylene vinylene; PT: polythiophene; PEDOT: poly-(3,4-ethylenedioxythiophene); PANI: polyaniline; PDPP-PD: polymer diketopyrrolopyrrole-phenylenediamine; PDI: perylene diimide; NDI: naphthalenediimide).

study of furan-based semiconducting materials could be considered one step closer to achieving green electronics. Oligofurans (with a mobility of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) have been widely studied as an active semiconductor material in OFET devices, and furan-substructures have been extensively used as building blocks within the backbone of conjugated materials. Sonar et al. combined furan and DPP and reported a series of furan-flanked DPP-based polymers with highest hole mobility of $3.56 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported for one of the polymers.^[71–77] Most of the resulting polymers demonstrated high-performance in OFET or solar cell devices, and some of them have even been processed from non-chlorinated solvents. These reports clearly revealed the potential of using furan in the construction of semiconducting materials for green electronics. Bao et al. also designed a DPP-based polymer (polymer diketopyrrolopyrrole-phenylenediamine, PDPP-PD) that introduced the imine group to the backbone to increase biodegradability under suitable conditions.^[9] From the structure, as shown in Figure 2, DPP and benzene were connected by an imine bond. This bond was quite stable in a neutral-pH condition; however, it was easily hydrolyzed with a catalytic amount of acid. This characteristic

allowed for the resulting degradability of the polymer. Not only were the DPP materials biodegradable, but so were other components in the device. Subsequently, this device showed both high hole mobility ($0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and excellent biodegradability. In DI water (pH = 7), the device was quite stable; however, it was totally disintegrated within 30 days in a buffer solution with a pH of 4.6.

Another class of promising semiconductors are derived from the π -conjugated molecules obtained from nature directly or via nature-inspired synthetic materials. In 2010, Irimia-Vladu et al. fabricated thin film transistors using a series of natural or nature-inspired materials that were all biodegradable and significantly less toxic than alternatives; the materials used included naturally occurring beta-carotene and indigo, indanthrene yellow G and indanthrene brilliant orange RF (both derivatives from natural anthraquinone), and PDI, a cosmetic color material.^[32] The transistors fabricated with these biodegradable materials demonstrated excellent mobility (10^{-4} to $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^[32] The indigo device, fabricated on a shellac substrate with AlO_x activated by the biodegradable tetratetracontane as the gate, was then transferred. Because of the highly

planar backbone structure and ability to be oxidized and reduced reversibly, the device showed ambipolar behavior with a hole and electron mobility of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[31] An important review, written by Irimia-Vladu et al., emphasized the H-bonding effects of these naturally occurring molecules as promising candidates for biodegradable materials.^[78] As shown in Figure 2, melanin, indigo derivative, alizarin, purpurin, PDI, and NDI all have extensive C = O groups, which could help form intramolecular and/or intermolecular H-bonding interactions. Although some of these molecules lacked intramolecular conjugation, the H-bonded intermolecularly connected materials rendered high-performance for organic electronic devices. Possibilities for future development were proposed using these types of biodegradable materials from nature or nature-inspired molecules. In fact, the H-bonding interaction has remained significant in various devices thus far. For example, Yu et al. have completed substantial work focused on improving the coplanarity of polymers by introducing analogous non-covalent interactions to enhance the mobility performance in OFETs.^[79] Bao et al. developed new polymers by introducing various moieties with H-bonding groups to the backbone; through these intermolecular H-bonding interactions, the materials have been successfully used in stretchable electronic devices.^[80] These types of materials have indicated great potential as biodegradable semiconductors in the future of green electronics.

2.2. Biodegradation Mechanisms in Materials

The biodegradation process entails the breakdown of organic matters by enzymes found in microbes, such as bacteria and fungi. Regarding the mechanism, biodegradation is generally divided into three different stages—biodegradation, biofragmentation, and assimilation.^[39] The first stage, biodegradation, occurs on the surface of materials when they are abandoned in an outdoor environment where various abiotic factors exist (i.e., intense sunlight, high pressure, high temperature, and various chemicals). All these factors induce changes in the mechanical, physical, and/or chemical properties. This stage includes mechanical degradation under compression, tension or shear forces, light degradation (for some photosensitive materials), thermal degradation (for materials with a low melting point or glass-transition temperature), and chemical degradation, such as oxidation. Although biodegradation is the first stage, in some cases, it occurs simultaneously with the second stage, which is called biofragmentation.

In biofragmentation, a lytic process occurs in which the chemical bonds are broken down, thereby producing several fragments such as oligomers or monomers. This step is further classified according to whether oxygen is or is not present during the process, and although the materials are broken down into fragments in either process, they are called aerobic and anaerobic digestion, respectively. Both processes generate some common by-products, such as carbon dioxide and water. The difference between aerobic and anaerobic digestion is that an anaerobic reaction generates methane during the degradation of organic materials. Furthermore, although aerobic digestion is typically complete in a shorter timeframe, it always increases the volume and mass of the materials. For this reason, anaerobic digestion does exceptional work in that both

the degradation and cleaning of waste are achieved in parallel. This is also the primary reason that anaerobic digestion is more commonly used in waste management systems. The generated methane is also used as a source of local, renewable energy.

After the first two stages are completed, the third stage, assimilation, begins to occur within microbial cells. Before entering the cell, certain products generated during the previous stage must complete a biotransformation reaction to ensure all resulting products are transported into the cell. For these molecules, a lack of permeable membrane carriers does not allow them to go through the cytomembrane; other molecules do not require this step because they can be easily transported into the cell by membrane carriers. Once all the products enter the cell, catabolic pathways are followed, and the products are ultimately oxidized into adenosine triphosphate and constitutive elements in the structure of the cell. Subsequent to this procedure, biodegradability is completed with the generation of non-harmful constituents. The newly produced biomass is ready for the next biocycling process.

While it might seem like a clear-cut procedure, the biodegradable process is a naturally complicated phenomenon. Biodegradation has proven to be difficult to carry out in a laboratory; therefore, a simulated process was conducted. As recently demonstrated in an excellent review paper by Bao et al., type I and type II degradations were brought forth, as shown in Figure 3-i.^[69] The reason for these two divisions was that it was unnecessary to let all the materials break down to their oligomers, monomers, and/or biomass and gases in a lab, especially for fundamental research. Type I materials were the widely studied candidates with transient behavior and primarily applied to the biomedical field (i.e., drug delivery and therapeutics).^[41] Type II materials were completely biodegradable, ultimately disappearing without a trace; therefore, these types of materials would be helpful in the creation of sustainable electronics. In this review, we will elaborate on the degradation method of biodegradable materials determined using laboratory methods.

In the lab, the degradation method applied most often is the dissolution method by choosing suitable solvents such as acidic, alkaline, and (some) enzymatic solutions or even simple dissolution in DI water. The main reactions occurring in a solution are hydrolysis and oxidation with various mechanisms under different conditions, generating small and harmless fragments. These fragments are then discarded in the environment to undergo further enzymatic degradation and microbial oxidation as occur in natural sources, for example, plant-based cellulose, alginate, dextran, animal-derived collagen, silk, and chitosan. The dissolution of metallic thin film electrodes or connects has been discussed in Section 2.1.2. Generally, they can dissolve in DI water (metal oxide or hydroxide), simulated body fluids (HBSS with pH values of 5–8), and acidic or alkaline solvents.^[43] In this way, although the dissolution rates vary, the similarity shown was that they could all be completely dissolved in corresponding solutions, generating soluble ionic products which can be easily removed or bio-resorbed in the environment.^[43]

For synthetic polymers, which generally contain some hydrolysable or oxidizable groups, as shown in Figure 3-ii, the degradation mechanism was hydrolysis, oxidation, or both in the presence of an acid, base, or some enzymes in solutions. As illustrated in Figure 3-ii(C,D), the representative hydrolysis and enzymatic

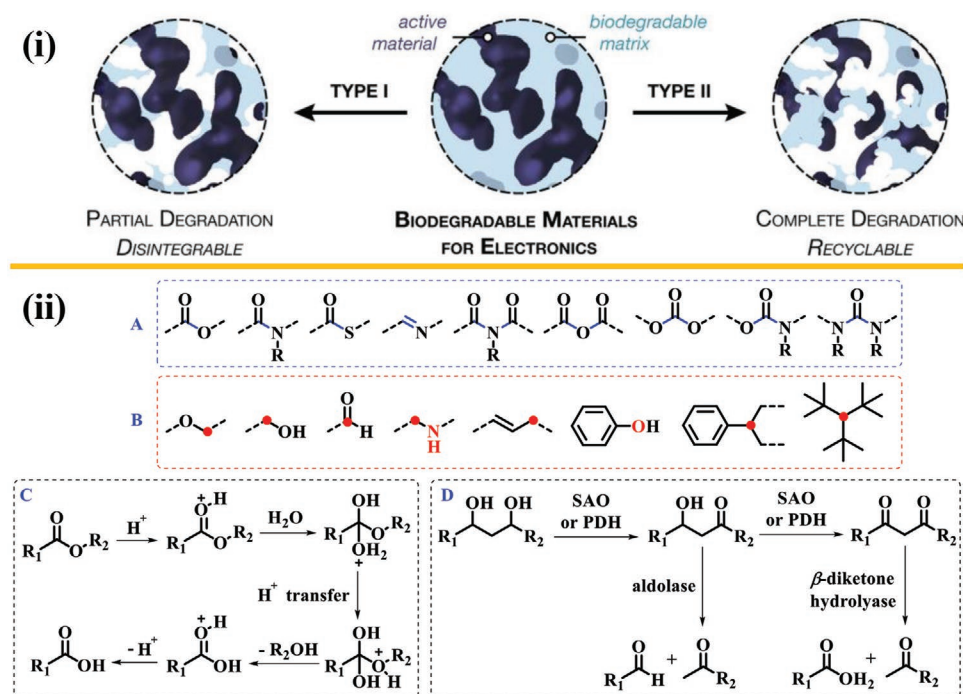


Figure 3. i) Two types of biodegradation proposed by Bao et al.: only matrix is fully broken down for Type I materials, while both matrix and active materials are fully broken down for Type II materials. ii) A: Moieties susceptible to hydrolysis; B: moieties susceptible to oxidation; C: acid catalyzed ester hydrolysis; D: polyvinyl alcohol enzymatic cleavage mechanism. Reproduced with permission.^[69] Copyright 2018, American Chemical Society.

cleavage processes demonstrated that the degraded products were ultimately non-toxic, and some were even recyclable compounds. There were many similar examples for these kinds of polymers described in a published book and review cited in the refs.^[69,81,82] Regarding the most important components, the semiconducting or conducting materials, degradation, hydrolysis, and oxidation were still the primary mechanisms because of the existing characteristic groups. However, as aforementioned, organic conjugated materials have been reported less in the literature for green electronics because C-C bonds are difficult to degrade.

A DPP-based polymer was reported by Bao et al., and the fabricated OFET device was completely degraded in acidic solution within 30 days.^[9] From the proposed mechanism, the polymer was not completely degraded; rather, it transformed into a colorless product. However, it still contained several conjugated structures and functional groups. The C-C bonds were not degraded in the least, which has proven to be a challenging subject to date. Although there have been a few reports regarding the enzymatic cleavage of C-C bonds, they have only been applicable to particular groups such as the sulphonamides, phosphonates, and ethers; therefore, a deeper understanding about this particular mechanism is essential.^[83]

2.3. Recent Development in Electronic Devices with Biodegradable Materials

2.3.1. Solar Cells

Solar energy is one type of renewable energy where full utilization is expected. Traditionally, a solar cell is the device used to convert

solar energy into electrical energy based on the photovoltaic effect. Currently, various solar cell technologies based on crystalline Si, thin film, perovskite, and organic semiconducting materials are rapidly developing and attaining high efficiency.^[84] Nonetheless, the research community in this field is still focusing great attention upon enhancing efficiency while focusing less attention and concern upon green solar cells with biodegradable materials, as well as focusing less attention upon recyclable photovoltaics for e-waste reduction. Nevertheless, a cradle-to-grave life-cycle assessment of solar cells reveals that both incineration and disposal in landfills cause a negative impact on the environment through the formation of photochemical oxidants, water depletion, and ecotoxicity.^[85] Comparatively speaking, biodegradable and recyclable solar cells are as important as high-efficiency solar cells and are highly desirable for sustainable development. As mentioned above, solar cells can be divided into several layers that mainly include a substrate, charge transporting layer, active layer, and electrode. Each layer can be used or combined with biodegradable materials. In this section, recent reports on new-generation solar cells (mainly organic solar cells [OSCs] and perovskite solar cells [PSCs]) consisting of one or more biodegradable layers are reviewed. It is worth mentioning here that recycling Si crystalline solar cell or thin film solar cell can recover 90% of the cover glass for use in new products, as well as 95% of the semiconductor materials for use in new solar modules.

Solar cells can be fabricated from biodegradable transparent substrates rather than traditional glass or a polyethylene terephthalate substrate. One example is cellulose, which can be used as a transparent, flexible substrate in OSCs owing to its high optical haze that can scatter the transmitted light and enhance solar cell performance.^[86] Cellulose is a low-cost biodegradable

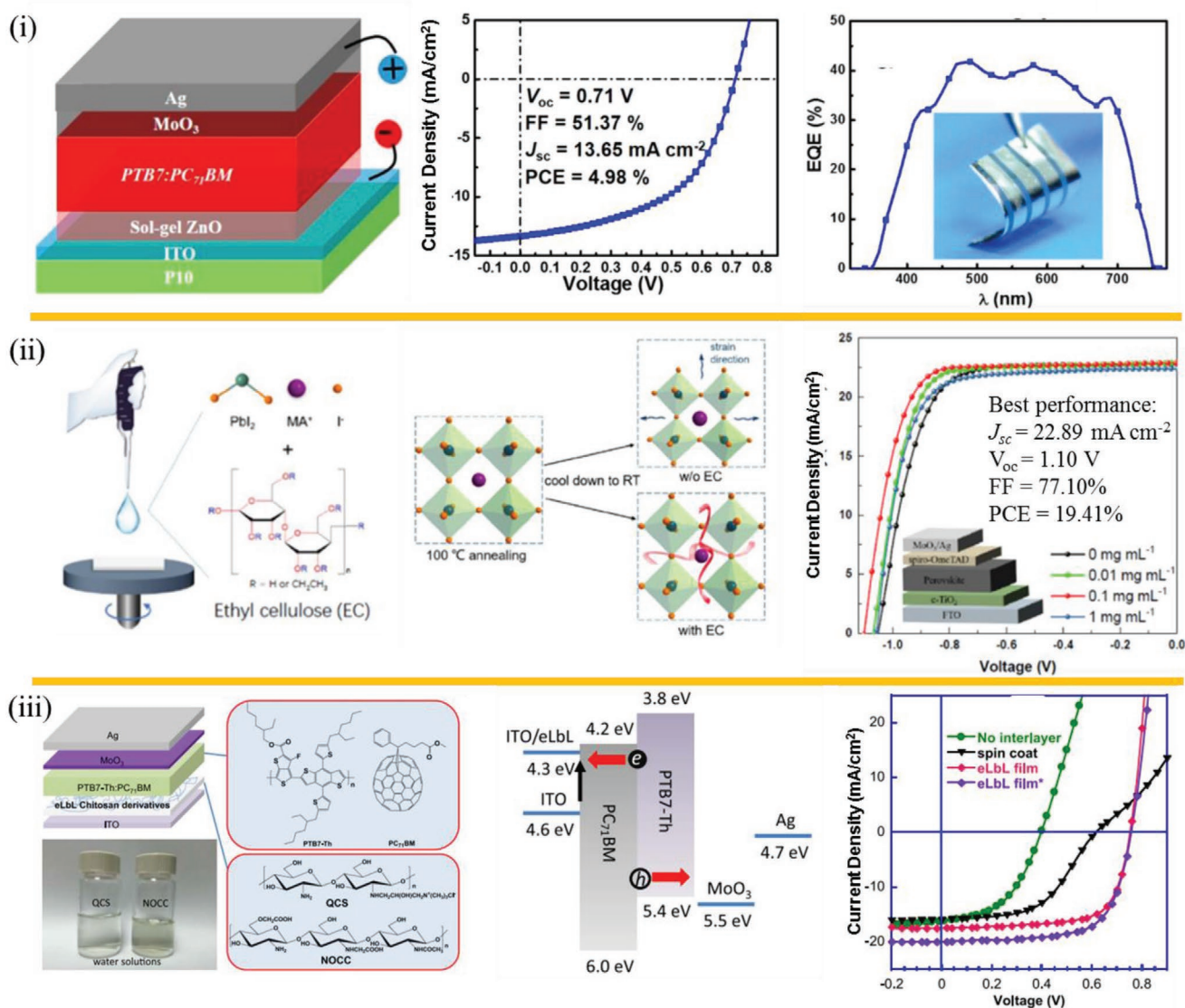


Figure 4. i) Organic solar cell (OSC) structure with cellulose-based paper as substrate and corresponding performance. Reproduced with permission.^[87] Copyright 2018, American Chemical Society. ii) Schematic illustration of ethyl cellulose (EC) passivation on perovskite defects and solar cell performance. Reproduced with permission.^[89] Copyright 2019, American Chemical Society. iii) OSC structure with chitosan derivatives as cathode interlayer materials and corresponding performance. Reproduced with permission.^[90] Copyright 2017, Elsevier.

material, and it is non-toxic and possesses biocompatibility properties. Notably, cellulose materials are readily degraded by bacteria in soil. Zhang et al. added tunicate cellulose nanocrystals (TCNCs) to O-(2,3-dihydroxypropyl) cellulose (DHPC) to synthesize a cellulose-based flexible paper substrate with a high transparency. Significantly, owing to the strong interfacial interaction between the TCNC and DHPC, the obtained substrate showed increases in the storage modulus and decomposition temperature, which were related to mechanically and thermally stable properties, respectively. Furthermore, a thin layer of ITO was deposited onto the cellulose-based paper and a solar cell was fabricated with a structure of paper/ITO/ZnO/PTB7-PC₇₁BM/MoO₃/Ag (PTB7:poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]; PC₇₁BM:[6,6]-phenyl

C71-butyric acid methyl ester), as shown in Figure 4-i. A power conversion efficiency (PCE) of 4.98% was achieved for the fabricated flexible inverted device.^[87] In another work, Cao et al. combined cellulose with AgNW to fabricate a transparent conductive film used as the substrate in PSCs. In addition, HNO₃ was applied post-treatment to enhance the bonding strength between the cellulose and AgNW. Accordingly, the obtained thin film was observed as 80% transparent with a sheet resistance of 29 Ω sq⁻¹, and the PCE of the PSCs was 4.49% with an open circuit voltage (V_{oc}) of 1.02 V, a short-circuit current density (J_{sc}) of 9.58 mA cm⁻², and a fill factor (FF) of 45.8%.^[88]

Chitosan was used as a biodegradable substrate in another report. Xiao et al. deposited AgNW onto an antioxidant acid-modified chitosan polymer and developed transparent bottom electrodes for the PSCs. The modified polymer could protect

the AgNW from the degradation of perovskite precursor without blocking the charge carrier drift. The sheet resistance of the composite was $171 \Omega \text{ sq}^{-1}$, and this initial sheet resistance was maintained even after 40 days, thereby indicating good stability of the chitosan-based electrode. Furthermore, the AgNW/chitosan composite was used as a bottom electrode to fabricate PSCs with the structure of AgNW/chitosan-based electrode/PEDOT:PSS/CH₃NH₃PbI₃/PCBM/Bphen/Al. The PCE was 7.9% with a V_{oc} of 1.04 V, J_{sc} of 21.0 mA cm^{-2} , and FF of 36.1%.^[91] The performance of the biodegradable substrate-based solar cells was not comparable to that of the conventional PSCs, but these works have been innovative and indicated great potential in the fabrication of biodegradable solar cells.

Transparency and haze are vital factors for light management in cellulose- or chitosan-based flexible substrates. To absorb sunlight more efficiently, substrates with high broadband transmittance and haze are required. Hu et al. developed a “top-down” approach to fabricate an anisotropic flexible paper that exhibits both high transparency and haze from pre-delignified wood materials through shear pressing. Significantly, a 14% enhancement in the PCE and an 18% improvement in the J_{sc} can be observed after the anisotropic transparent paper is coated onto a GaAs solar cell, demonstrating efficient light management by the anisotropic paper.^[92] The substrate in this work may be a good option for the fabrication of high-performance biodegradable OSCs and/or PSCs.

In addition to utilizing biodegradable cellulose and chitosan materials as substrates, they could also be used to passivate the defects of the PSCs, which act as a charge recombination center and suppress the charge-transfer, or interfacial layer, in OSCs. Bao et al. introduced the low-cost and biodegradable ethyl cellulose (EC) into perovskite precursor with different concentrations. The H-bonding formed between the EC and perovskite effectively passivated the charge defect traps, thereby increasing the PCE from 17.11% to 19.41% (Figure 4-ii).^[89] Wang et al. deposited chitosan derivatives on ITO to act as cathode interlayer materials to fabricate OSCs in which PTB7-Th:PC₇₁BM (PTB7-Th:poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-2-carboxylate-2,6-diyl)]) was selected as the active layer material. The work function of the ITO was successfully decreased from 4.6 to 4.3 eV owing to the formation of an ordered layer-by-layer structure and interfacial and molecular dipoles, which facilitated the charge-transfer. The solar cell efficiency approached 10.18% with a chitosan derivatives interlayer, as shown in Figure 4-iii.^[90] Chitosan was also used as an interfacial layer to modify a ZnO electron transport layer (ETL) for an OSC with PTB7-Th:PC₇₁BM as a bulk-heterojunction (BHJ) active layer, demonstrating an efficiency of 7.54%.^[93]

Based on the above discussion, biodegradable materials are mostly used as substrates, additives, or interlayers in solar cells. However, the back electrodes in solar cells still consist of traditional metals such as Au, Ag, Cu, Al, or their corresponding alloys. These metal electrodes are corrosion-resistant with high conductivity but are typically costly and rare.^[94] Mg, Mo, manganese (Mn), Fe, W, and Zn are environmentally friendly and are metabolized under appropriate physiological conditions, as mentioned in Section 2.1.2. Among these, Mg exhibits a work

function of 3.7 eV, conductivity of $22.6 \times 10^6 \text{ S m}^{-1}$, is biodegradable, and can be dissolved in water.^[95] Nevertheless, Mg is rarely used in solar cells, probably owing to its easy oxidation and reaction in air. Considering the trade-off between biodegradability and chemical stability, such transient metals can be used for specific devices with special designed lifetime, such as transient electronic devices. Carbon-based materials may be alternatives for noble metals, owing to their low-cost, high-stability, and hydrophobic and biodegradable natures. Carbon electrode materials have been applied to PSCs, and the PCE approached 15.7%.^[96] The screen-printing, doctor-blading, rolling-transfer, and hot-pressing deposition methods are used for carbon electrodes.^[97] Significantly, carbon materials can replace the hole-transport layer (HTL), allowing for the large-scale fabrication of PSCs without a hole-transport layer. Despite this development, there is still no report regarding an assessment for the biodegradability of active (light-absorbing) materials or the modification of materials to facilitate biodegradation. These areas will need to be developed in the future to make a truly biodegradable solar cell.

2.3.2. OFETs

OFETs are the key components of many organic electronic devices.^[98–100] OFETs fabricated with biodegradable materials show promise in the effort to solve the waste issue of field-effect transistors (FETs). An OFET is usually made up of a substrate, gate electrode, semiconductor, dielectric, and source/drain electrodes. In fact, each layer can be deposited with suitable biodegradable materials to make biodegradable OFETs.

A traditional FET is fabricated on a hard substrate. Although such a device possesses high charge carrier mobility, there remains a problem associated with its biodegradability. Therefore, selecting a proper biodegradable substrate is the first step in fabricating biodegradable OFETs. One safe biodegradable material for substrates is poly(lactic-co-glycolic acid) (PLGA). It is composed of two monomers, lactic acid, and hydroxyacetic acid, which are randomly polymerized. Approved by the Food and Drug Administration (FDA) of the United States, it is widely used in pharmaceutical, medical, and industrial fields because of its biocompatibility, biodegradability, non-toxicity, and feasibility as capsules and membranes. Gradually, it is making its way into the field of green electronics. Bao et al. first reported a thin film p-channel 5,50-bis-(7-dodecyl-9H-fluoren-2-yl)-2,20-bithiophene transistor fabricated on a PLGA substrate, as shown in Figure 5-i, with a PVA gate dielectric, high hole mobility of $0.253 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and an on/off ratio as high as 9.4×10^3 .^[101] The similar OFET device fabricated with the same semiconductor but Si substrate achieved a hole mobility of $0.39 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[102] In addition, PLGA has also been utilized in organic electrochemical transistors as a biodegradable substrate,^[103] water-gated OFET,^[104] and transient hydration sensor.^[105]

As in solar cells, cellulose has been used as a substrate in OFETs. As a water-insoluble macromolecular polysaccharide, cellulose has been utilized as a biodegradable material in green electronics.^[109] Cellulose-based substrates have the advantages of good mechanical flexibility and chemical dissolvability.

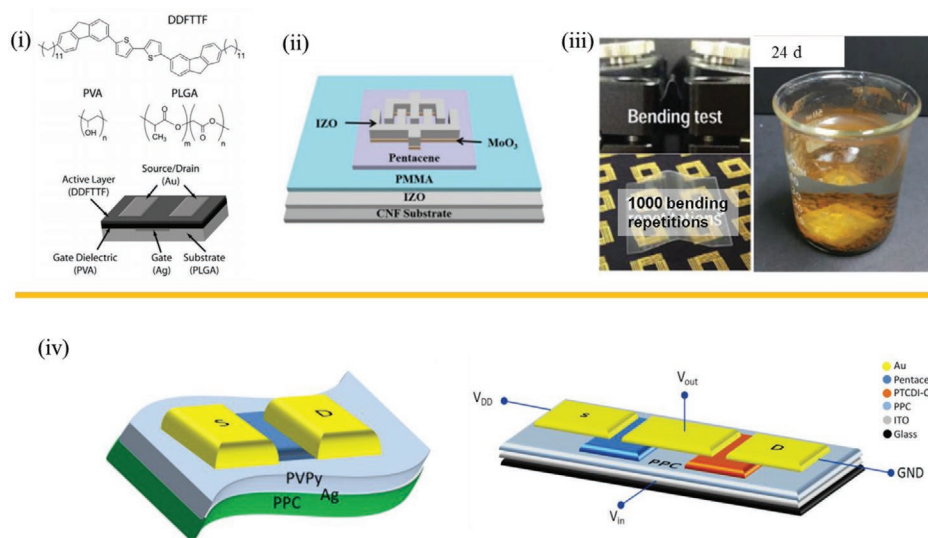


Figure 5. Schematic diagrams of biodegradable organic field-effect transistors (OFETs): i) poly(lactic-co-glycolic acid) (PLGA) Reproduced with permission.^[101] Copyright 2010, Wiley-VCH, and ii) cellulose nanofibrillated fiber (CNF) substrate. Reproduced with permission.^[106] Copyright 2018, Wiley-VCH. iii) Bending test of starch paper substrate by adding 0.5 wt% polyvinyl alcohol (PVA) and 5 wt% of crosslinker (left), and biodegradability test by immersing starch paper in fishbowl water for 24 days (right). Reproduced with permission.^[107] Copyright 2018, Wiley-VCH. iv) Schematic diagrams of OFETs based on biodegradable polypropylene carbonate (PPC) as substrate (left) and dielectric layer (right). Reproduced with permission.^[108] Copyright 2018, Nature Publishing Group.

Furthermore, they have been obtained easily and at low-cost. Recently, Bao et al. have reported an ultrathin, ultralightweight cellulose substrate for transient electronics.^[110] Not only was this substrate proven to be transparent, flexible, and biodegradable, but it was also more tolerant to high temperature, water, and organic solvents than many other biodegradable substrates. A fully disintegrable and biocompatible polymer transistor with a low-operating voltage was successfully fabricated on an ultrathin cellulose (800-nm-thick) biodegradable substrate. In addition, by applying Fe electrode, the OFET device exhibited a comparable hole mobility with that of a device fabricated with Au electrode ($0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for Fe vs $0.34 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for Au). Another interesting application for a cellulose substrate was reported by Ju et al.^[106] Using pentacene as an active organic semiconducting layer and MoO_3 -buffered indium zinc oxide (IZO) electrodes on a biodegradable nanofibrillated fiber substrate, the transistor exhibited good performance, as shown in Figure 5-ii. With a transmittance greater than 70% and a preeminent saturation mobility of $1.40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, the device exhibited good mechanical flexibility after the bending cycle.

Paper, consisting of cellulose, has also been used as a substrate for OFETs. Gao et al. reported a flexible poly(3-hexylthiophene) (P3HT) organic transistor with a chitosan smoothing layer, Au source/drain electrodes, and a reusable ion gel dielectric layer fabricated on a paper substrate.^[111] Besides good mechanical flexibility and a low-operating voltage (approximately 2 V), the device exhibited an on/off ratio of 10^4 and a high mobility of $0.97 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This hole mobility value is even comparable with that of devices based on P3HT fabricated on flat substrates ($1.1 \pm 0.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^[112] However, the roughness and non-transparency of the commercial paper were drawbacks that would limit its large-scale application in OFETs. Although transparent paper has been reported, it required an extra planarization procedure. Starch paper has overcome the

drawbacks mentioned above and could be a potential material for the next generation of OFETs. Lee et al. demonstrated OFETs based on a starch paper substrate using different organic semiconductors with the gate dielectric parylene-C, and these OFETs performed well.^[107] Additionally, it was found that the mechanical property of this substrate could be improved by adding 0.5 wt% of PVA and 5 wt% of a crosslinker that could bind to the PVA, as shown in Figure 5-iii. More importantly, the starch paper was fully biodegraded after immersion in fishbowl water for 24 days, suggesting an alternative to the conventionally non-biodegradable plastic substrates.

Another noteworthy environmentally friendly material is polypropylene carbonate (PPC). PPC is a biodegradable aliphatic polyester product of the copolymerization of CO_2 and propylene oxide under catalysis with a Zn complex. Thus, the synthesis of this material not only decreases the greenhouse gas, CO_2 , but it also makes a valuable product. Recently, Chu et al. reported the potential of PPC for use in OFETs as the substrate and dielectric layer, as shown in Figure 5-iv.^[108] The pentacene organic transistor employing PPC dielectric demonstrated a mobility of $0.14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, an on/off ratio of 10^5 , and an operating voltage of 60 V. When the PPC was used as the substrate, the device performance of pentacene-based OFET was enhanced to $0.27 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This result indicated the great potential application of biodegradable PPC as both substrate and dielectric materials. The PPC sheet also exhibited 92% transparency and good mechanical flexibility, thereby demonstrating its potential in OFET-based electronic displays.

Regarding gate dielectrics, the demand for high- k -value materials with biocompatible and non-toxic properties has increased for use in green OFETs. Concerning these conditions, natural materials existing in plants, insects, and animals could provide clues. Many new gate dielectric materials have been introduced, and their OFET devices exhibited good performances.

Natural silk has attracted research interest owing to its excellent properties of non-toxicity, mechanical flexibility, solution-processability, and biodegradability. Several works on OFETs that used different semiconductors demonstrated the outstanding dielectric property of natural silk.^[113–117] One significant work reported a high-performing pentacene OFET fabricated on a PEN substrate with silk gate dielectrics.^[117] A mobility of $23.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained under a low-operating voltage of -3 V , effectively outclassing inorganic dielectric SiO_2 a hundred times over. Its excellent charge transport characteristic was attributed to the improved crystallization of pentacene by silk fibroin (SF) and low interface scattering between the SF and pentacene.

Keratin protein, a type of structural protein found in animal hairs and feathers, has proven itself as a feasible material in green OFETs because of its degradation characteristic with the existence of peptide bonds. Chicken feathers, which contain 90% keratin protein, have been considered useless and treated as garbage in the food industry. Recently, Ko et al. demonstrated a valuable use for chicken feathers as the gate dielectric layer in biodegradable OFETs.^[118] The chicken feathers were first dissolved in a urea and cysteine solution under an alkaline condition and then distilled and centrifuged; a pure keratin solution was acquired for device fabrication. The metal/insulator/metal capacitor devices with keratin thin film exhibited a low leakage current density of $1.2 \times 10^{-7} \text{ A cm}^{-2}$. Based on the P3HT active layer with a keratin dielectric layer (500-nm-thick), the OFET device exhibited a high on/off ratio of 1.19×10^5 , saturation mobility of $2.323 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and low threshold voltage of -1 V , as shown in **Figure 6-i**. Although the performance is not high, this value is much higher than that of device fabricated with SiO_2 gate dielectric ($1.08 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) under completely same fabrication procedures and characterization conditions. Remarkably, keratin protein was fed to fish, thereby introducing a new degradation method. Human hair could also be an ideal source of keratin protein. Leong et al. reported a p-channel poly[4-(4,4-dihexadecyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)-alt[1,2,5]thiadiazolo[3,4-c]-pyridine] (PCDTPT) thin film transistor with a human hair keratin dielectric layer with a low-operating voltage.^[119] The keratin dielectric layer had a capacitance as high as $1.27 \mu\text{F cm}^{-2}$. The transistor exhibited good performance with a mobility value of $0.35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (**Figure 6-ii**). Although the performance is slightly lower than that of device fabricated with SiO_2 dielectric layer ($0.94 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), the keratin exhibited a good degradability in ammonium hydroxide solution.

Other naturally biodegradable materials, including cellulose, chitosan, chicken albumen, and gelatine, were discussed in reports and used as gate dielectrics.^[120–124] Stadlober et al. introduced an ultrathin hybrid high- k dielectric layer into a pentacene OFET.^[120] The cellulose dielectric layer was obtained by spin-coating desilylation of trimethyl-silyl cellulose and regenerated by exposing it to hydrochloric acid vapors. The device demonstrated low leakage currents and a mobility of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Huang et al. used ultrasmooth wood-derived cellulose nanopapers (WCNs) as the gate dielectric in organic synaptic transistors.^[121] The WCNs showed an excellent ionic conductivity of $7.3 \times 10^{-4} \text{ S m}^{-1}$ and a lateral capacitance of 18.65 nF cm^{-2} at 30 Hz . Significantly, the organic synaptic transistor successfully mimicked synaptic behaviors at a low-operating voltage of 1.5 V . Ko et al. investigated a blend of Y_2O_3 nanoparticle/chitosan as a

gate dielectric and demonstrated an improvement in device performance compared with that of the single chitosan dielectric layer.^[122] After mixing the Y_2O_3 nanoparticle with the chitosan, the leakage current decreased and the on/off ratio increased by 100 times. The P3HT OFET was of bottom-gate top-contact structure and used Au/Cr electrodes that exhibited a low-operating voltage, an on/off ratio of approximately 10^5 , and a mobility of $8.53 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Liu et al. applied gelatine to the gate dielectric of the pentacene OFET, and it exhibited good charge transport characteristics in ambient air.^[123] The mobility was $16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a voltage of 5 V in the saturation regime. This high mobility could be attributed to the negatively charged ions produced by the interaction between water and the polar hydroxyl in the ammoniac acids of the gelatine.

Furthermore, synthesized biodegradable materials, such as poly-methacrylate tannic acid (PMTA), PVA, poly(methyl methacrylate) (PMMA), and poly(4-vinylphenol) (PVP), have been used as gate dielectrics.^[125–127] Kim et al. reported a pentacene OFET with PMTA as the gate dielectric and Au as the source/drain electrodes.^[125] The PMTA dielectric exhibited a good electrical breakdown strength of 5.4 MV cm^{-1} . The OFET exhibited a mobility of $0.229 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at a gate voltage of -20 V . Owing to the stable structure of PMTA, the device was hysteresis free. An OFET fabricated on a PVA substrate with a PMTA gate dielectric could fully dissolve in a PBS solution ($\text{pH} = 7.4$) at 35°C after 8 days, which indicated excellent degradability. Iyer et al. demonstrated a high-performance OFET using a conjugated molecule, octadecyl-amine substituted 1,4,5,8-NDI as the semiconductor, and PVA as the dielectric.^[126] Huang et al. reported stable OFETs with net-structured cross-linked PVP inserted between two ultrathin PMMA layers as polymeric dielectrics. The dielectric with a core-shell-like structure exhibited better electrical insulation, which allowed for a 4 V-driven flexible OFET with a high mobility of $0.72 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and excellent bias-stress stability in air.^[127]

A semiconducting active layer has been highly desired for use in biocompatible and biodegradable materials with high mobility for the fabrication of green OFETs. A PDI OFET with a glucose gate dielectric exhibited the highest mobility of $0.01\text{--}0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[32] A natural indigo-based OFET was fabricated using natural shellac resin substrates, and its balanced electron and hole mobility were $1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, demonstrating potential for the fabrication of green electronics with biodegradable and non-toxic semiconductors.^[128] Similar with solar cells, few reports used biodegradable materials as active layer in OFETs. Natural active materials are with good biodegradability but poor performance, meanwhile, synthesized active materials perform reversely. Alternatively, molecular design through combining the advantages of natural and synthesized active materials can be the promising strategy to enlarge the selectable biodegradable active materials for OFETs. The reported performance of OFETs with biodegradable materials is summarized in **Table 1**.

2.3.3. LEDs

Optoelectronic devices have played a crucial role in illumination, mobile devices, and smart homes. The use of

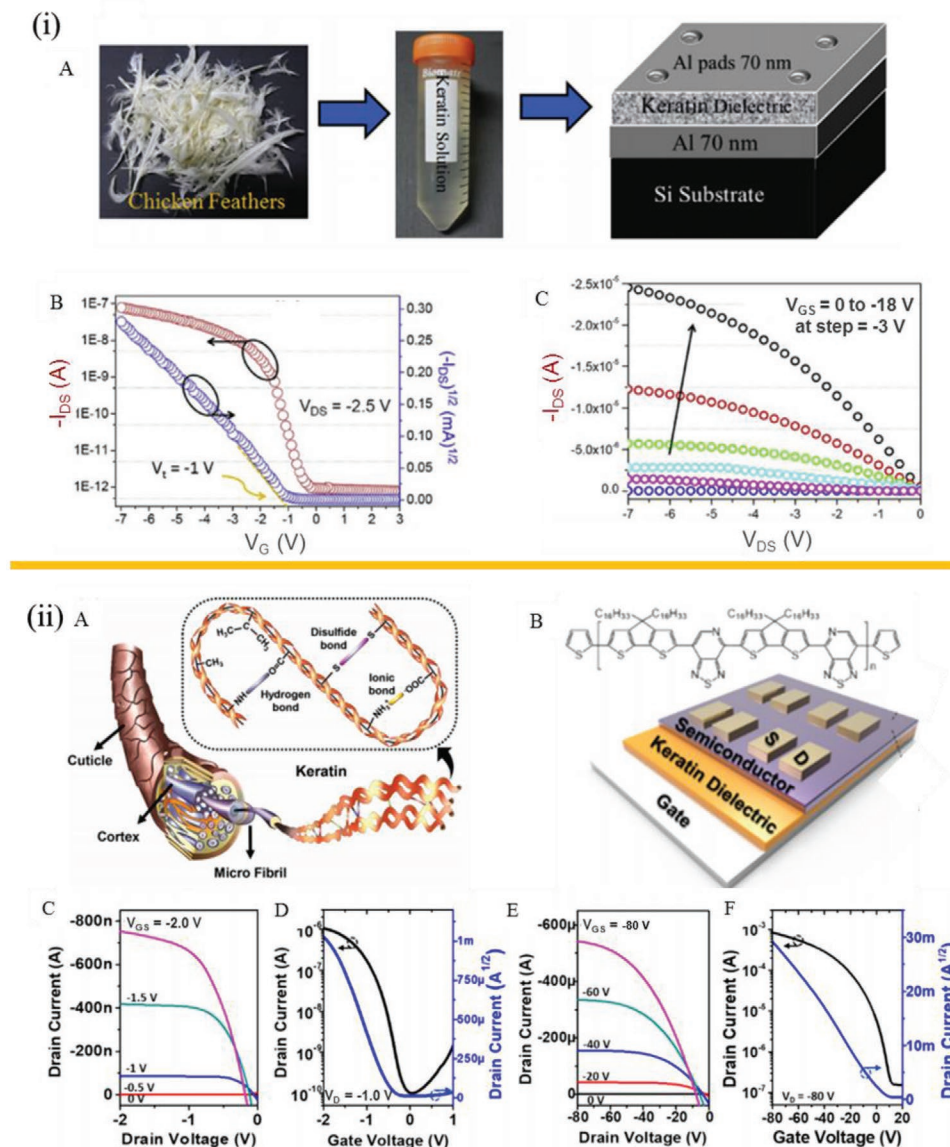


Figure 6. i) A: Device structure with keratin protein as dielectric layer. B,C: Transfer and output characteristics of keratin dielectric-based organic thin-film transistor (OTFT). Reproduced with permission.^[118] Copyright 2017, Elsevier. ii) A: Schematics of keratin from human hair and various chemical bonds in keratin. B: Bottom-gate top-contact p-channel poly[4-(4,4-dihexadecyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)-alt[1,2,5]thiadiazolo[3,4-c]pyridine] (PCDTPT)/keratin TFT and molecular structure of PCDTPT. C,D: Output and transfer characteristics of PCDTPT/keratin TFT. E,F: Output and transfer characteristics of reference PCDTPT TFT on SiO₂ dielectric layer. Reproduced with permission.^[119] Copyright 2017, American Chemical Society.

biodegradable materials in light-emitting devices, such as LEDs and light-emitting electrochemical cells (LECs), could enable the fabrication of renewable and eco-friendly displays for healthcare electronic devices, as well as other sustainable applications. Several kinds of biodegradable materials such as naturally occurring materials of living organisms (e.g., eumelanins,^[131] DNA,^[132–134] mucin,^[135] serum albumin,^[136] and fluorescent proteins^[137]) and synthetic or hybrid-natured materials (e.g., silk,^[138,139] cellulose,^[140–146] carbon-based materials,^[147–151] and biodegradable polymers^[151–154]) have been reported for use in individual components of light-emitting devices. Recent progress in this field has mainly focused on how to apply biodegradable materials to light-emitting devices properly, thereby

allowing for the replacement of expensive and unsustainable components without any obvious loss in performance. This section introduces the most used and widely studied biodegradable materials in LEDs, focusing on their performance, application, and feasibility with different types of devices.

Inorganic LEDs: Inorganic LEDs (ILEDs) are semiconductor-based light sources made of a compound that combines elements such as indium (In), arsenic, gallium, phosphorous, and nitrogen. When a forward bias is applied to ILEDs, the injected holes and electrons are combined with the electrons in the n-region and holes in the p-region (near the p-n junction) to generate fluorescence (i.e., spontaneous emission). The energy states of electrons and holes in different semiconductor

Table 1. Summary of the performance of reported OFETs with biodegradable materials.

Biodegradable materials	Functional layer	Device structure	μ (cm ² V ⁻¹ s ⁻¹)	I_{on}/I_{off}	Ref.
PLGA	Substrate	BGTC	0.253	9.4×10^3	[101]
tascPLA	Substrate	BGTC	0.58	–	[129]
Cellulose	Substrate	BGTC	0.12	$>10^4$	[9]
CNF	Substrate	BGTC	1.40	10^5	[106]
Cellulose paper	Substrate	BGTC	0.97	10^4	[111]
Starch paper	Substrate	BGTC	0.37	4.9×10^5	[107]
PPC	Substrate	BGTC	0.27	10^4	[108]
Shellac resin	Substrate	BGTC	1×10^{-2}	–	[128]
Shellac resin	Substrate	BGTC	0.4	10^5	[130]
Silk fibroin	Gate dielectric	BGTC	10	10^3	[113]
Silk fibroin	Gate dielectric	BGTC	0.39	9.3×10^2	[114]
Silk fibroin	Gate dielectric	BGTC	0.01	10^4	[115]
Silk fibroin	Gate dielectric	BGTC	23.2	3×10^4	[117]
Chicken feather keratin	Gate dielectric	BGTC	2.323×10^{-3}	1.19×10^5	[118]
Human hair keratin	Gate dielectric	BGTC	0.35	1.1×10^4	[119]
Cellulose	Gate dielectric	BGTC	0.1	–	[120]
WCNs	Gate dielectric	LCFET	1.25	–	[121]
Y ₂ O ₃ nanoparticle/chitosan	Gate dielectric	BGTC	8.53×10^{-2}	10^5	[122]
Gelatine	Gate dielectric	BGTC	16	–	[123]
Chicken albumen	Gate dielectric	BGTC	0.13	10^4	[124]
PMTA	Gate dielectric	BGTC	0.229	–	[125]
PVA	Gate dielectric	BGTC	1.0	10^2	[126]
PVP	Gate dielectric	BGTC	0.72	2.3×10^4	[127]
PDI	Semiconductor	BGTC	0.01	10^5	[32]
β -carotene	Semiconductor	BGTC	4×10^{-4}	–	[32]
Vat Yellow 1	Semiconductor	BGTC	0.012–0.015	–	[32]
Vat Orange 3	Semiconductor	BGTC	1.75×10^{-3}	–	[32]
Indigo	Semiconductor	BGTC	0.01	–	[128]

PLGA, poly(lactic-co-glycolic acid); tascPLA, three-arm stereocomplex polylactide; CNF, cellulose nanofibrillated fiber; PPC, polypropylene carbonate; WCNs, wood-derived cellulose nanopapers; PMTA, poly-methacrylate tannic acid; PVA, polyvinyl alcohol; PVP, poly(4-vinylphenol); PDI, perylene diimide; BGTC, bottom-gate top-contact; LCFET, laterally coupled field-effect transistor; μ , hole/electron mobilities; I_{on}/I_{off} , on/off current ratios.

materials are different, which causes different energy released by the recombination. The more energy that is released, the shorter the wavelength of light that is emitted.^[155]

In the past 10 years, white ILEDs (WILEDs) have significantly developed and obtained a place in the lighting market. They have been widely used for illumination, front automotive lights, signaling, backlighting of liquid crystal displays, etc.^[156] There are five components integrated in commercial WILEDs: electronic driver, heat dissipating system, emitting chip, packaging system, and components for light extraction and color conversion. Because the electronic driver, heating dissipating system, and emitting chip of commercial WILEDs are fabricated with well-established methods, recent research on biodegradable materials applied to WILEDs and white hybrid LEDs mainly focuses on the substitution of these components for light extraction, color conversion, and typical packaging systems.

The color down-converting material plays a decisive role in white LEDs because it determines the color temperature, color quality, and brightness of the device. In choosing a biodegradable material for use in a color down-converter, it must not only meet the requirements for luminescence and optical features, but it must also be compatible with the packaging system. Fluorescent proteins (FPs), which were already successfully utilized in bio-lasers as color converters,^[157] were first reported as the color down-converters in white hybrid LEDs by Costa et al. in 2015, as shown in **Figure 7-i**.^[137] This new matrix, which combines a branched polymer (trimethylolpropane ethoxylate) and a linear polymer (polyethylene oxide), was developed to remedy the low mechanical stability of the origin hydrogel under the conditions of moisture and high temperature. An elastomeric compound was created from stabilized FPs without cross-linking reactions, and it exhibited a good performance of approximately 90% transmittance over the whole visible range

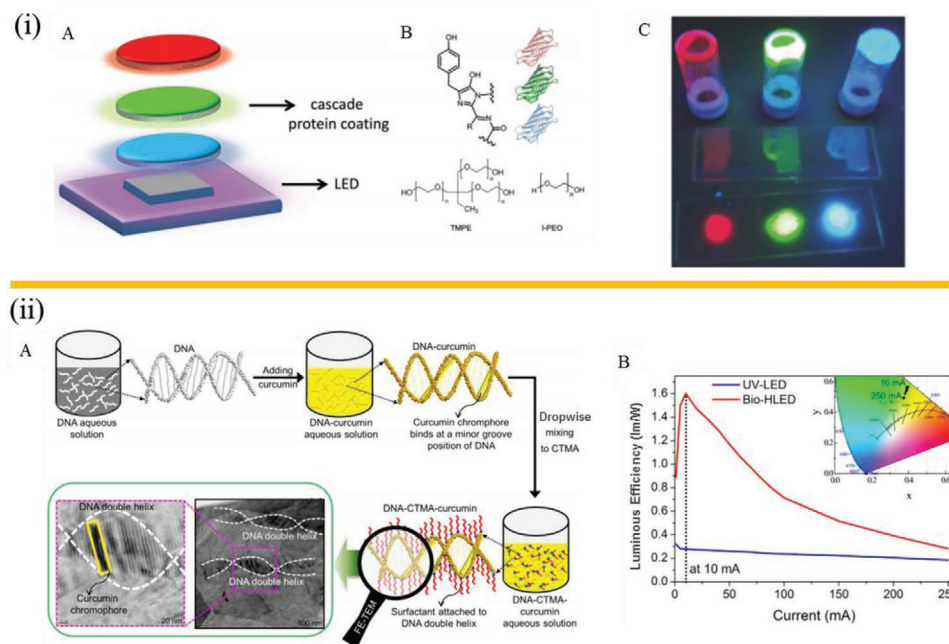


Figure 7. i) A: Architecture of bio-hybrid inorganic/organic light-emitting diodes (LEDs) with cascade coating based on red, green, and blue fluorescent proteins (FPs). B: Chemical structures of chromophores. C: Photograph of protein-based gels and rubber-like materials upon excitation at 310 nm. Reproduced with permission.^[137] Copyright 2015, Wiley-VCH. ii) A: Processing steps of DNA–cetyltrimethylammonium (DNA-CTMA)–curcumin aqueous solution. B: Comparison of luminous efficiency between DNA-curcumin-based LED and normal UV-LED. Reproduced with permission.^[160] Copyright 2016, Nature Publishing Group.

and withstood temperatures as high as 100 °C. Further progress in this field was made by Nizamoglu et al., who reported a creative method to achieve a combination of FPs and blue LED chips (450 nm) without a polymer matrix.^[158] The fabrication of these devices was carried out by drying the aqueous solution (40 °C for 25 min) with a mixture of enhanced-green FPs and monomeric Cherry protein in a glass reservoir; the devices were finally placed on blue LEDs as the color down-converter. Later, Kumar et al. reported a bovine serum albumin (BSA)-based biophosphor,^[159] which was obtained by mixing natural BSA and water-soluble carbodiimide 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide. The cross-linked BSA, with two or three fluorescent dyes, was coated on UV-LEDs as the color down-converter, and the encapsulation was cascade-like. The hydrogel rendered an average thickness of 0.5 mm and CIE color coordinates of (0.36, 0.37).

In 2016, Reddy et al. reported a crystalline DNA-based complex used as the color down-converting material for LEDs.^[160] The DNA double helix structure was first modified with curcumin chromophore and then transformed into its crystalline form. The LEDs fabricated with thick crystalline DNA complex on a UV-LED chip exhibited green emission and a maximum luminous efficiency of 1.6 lm W⁻¹ with a stability of a few hours when driven at the current of 10 mA (Figure 7-ii). Because of the novelty and low-cost of the curcumin in this method, the DNA-based color down-converting material could be appealing and cost-effective in the fabrication of devices.

Organic LEDs: In the past 20 years, with the development of high-purity organic conductive polymers, much research on organic/polymer LEDs was conducted and significant progress

was made by scientists. OLEDs have a high luminous efficiency, simple structure, and low manufacturing cost. With an improved transport layer and continuous optimization of this structure, the technology should readily advance in the application to display devices. Generally, OLEDs have exhibited a sandwich-like structure, including a substrate, anode, hole injection layer, HTL, emitting layer, ETL, electron injection layer, and metal cathode. The balance of the hole and electron injection layers has proven crucial for efficient OLEDs, owing to the structure and mechanism of hole-electron recombination. To date, several individual components of OLEDs that were made with biodegradable materials have been reported, and they will be introduced in subsequent sections.

Cellulose, with its excellent thermal stability, recyclability, sustainability, and flexibility, has become an attractive material for the substrates and/or encapsulations of OLEDs.^[142] To meet the requirements of device fabrication, it has been found that cellulose-based substrates must exhibit a low roughness and low coefficient of thermal expansion (CTE) to avoid unreliability and damage to the active materials during the fabrication process under high temperatures. Bacterial-derived cellulose (BC) containing nanofibers with a low CTE and high tensile strength was first reported and applied as a substrate for OLEDs by Yano et al.^[161] The substrate was prepared with bacterial *Acetobacter xylinum* FF-88 and impregnated acrylic resin, which exhibited a light transmittance loss of less than 8% compared with that of acrylic resin, and even the nanofiber content was as high as 70%. Later, they produced acrylic resin with 5% BC that exhibited suitable flexibility and mechanical properties. Compared with that of the individual resin, the transmission of

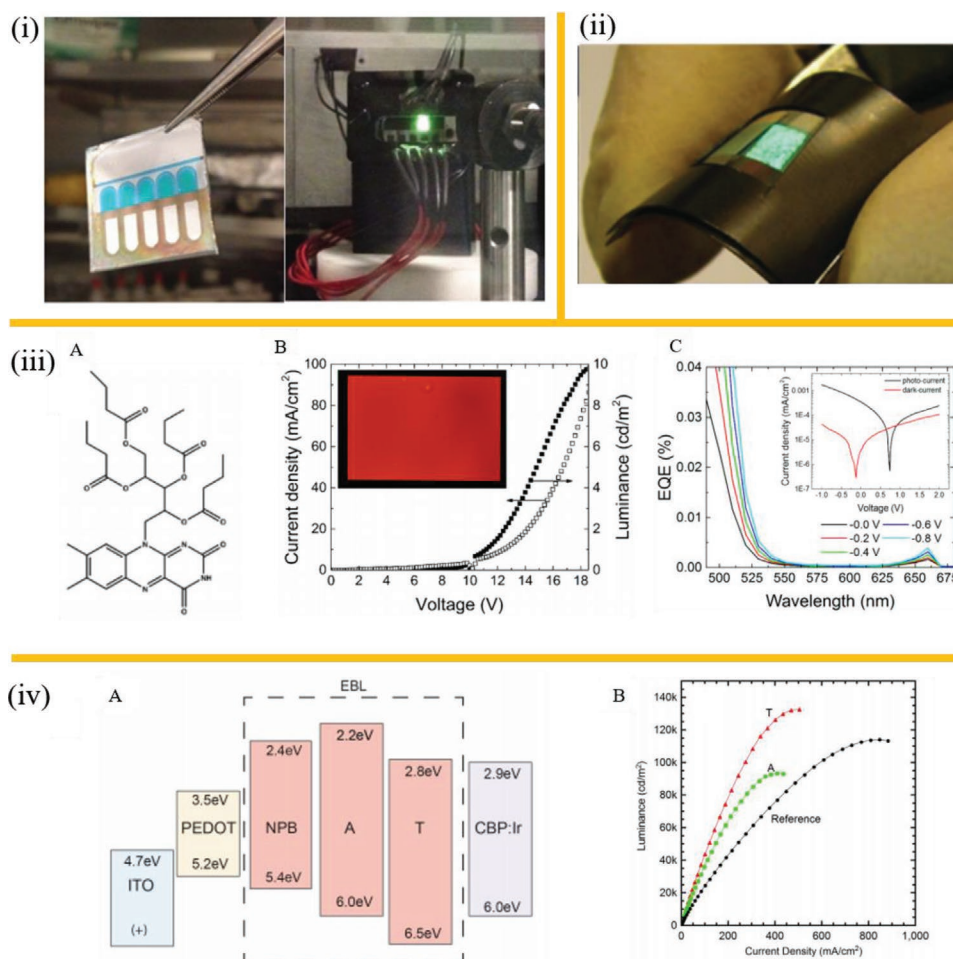


Figure 8. i) Photographs of organic light-emitting diodes (OLEDs) on cellulose nanocrystal (CNC) substrate mounted on glass (left) and illuminated OLED on CNC substrate (right). Reproduced with permission.^[143] Copyright 2014, American Institute of Physics. ii) Digital images of working flexible OLEDs on bacterial-derived cellulose/castor oil polyurethane (BC/PU) composite. Reproduced with permission.^[163] Copyright 2015, Royal Society of Chemistry. iii) Molecular structure of riboflavin-tetra butyrate (RFLT); current density and voltage characteristics; EQE of the RFLT-poly(9-vinylcarbazole) bilayer photodiode. Reproduced with permission.^[166] Copyright 2017, American Chemical Society. iv) Energy levels of DNA-based OLED; luminance and current density characteristics. Reproduced with permission.^[167] Copyright 2014, Nature Publishing Group.

the composite showed a loss of only 8.7% with good bending properties.^[162] However, as a derivative of petroleum, the aforementioned resin was not perfectly biodegradable. In 2014, Kipelen et al. developed OLEDs with a cellulose nanocrystals (CNC)-based substrate (Figure 8-i).^[143] Two years later, Pinto et al. reported a thin film that combined BC with castor oil polyurethane (PU) and exhibited a high transmittance of 80% and good stability (Figure 8-ii).^[163] Recently, Mashkour et al. reported multi-walled CNTs (MWCNTs)-coated cellulose as electrically conductive cellulose nanopapers (EC-CNPs).^[164] The effects of various drying and stabilization methods on the properties of EC-CNPs were compared for further application. Cellulose could also be used for the encapsulation material of OLEDs. Because moisture and oxygen are the major barriers for encapsulated OLEDs, Nguyen et al. used cellulose acetate as the encapsulation material, owing to its transparency, low-cost, and hydrophobicity.^[165] A comparison between the stability of both encapsulated and standard OLEDs indicated that the OLEDs encapsulated with cellulose acetate exhibited a stability that was

2 weeks longer than that of the corresponding standard devices, thereby demonstrating the potential of cellulose acetate as the encapsulation material of OLEDs.

The key parameters in a satisfactory transparent electrode for OLEDs are good conductivity, transmittance, and feasibility in flexible devices. SF was first reported as the material for an electrode implemented with a composite based on an AgNW mesh by Sun et al. in 2015.^[168] To smooth the film surface and improve adhesion, an AgNW mesh was embedded into an SF matrix by first drop-casting AgNW solution onto a polished Si wafer, followed by dropping SF solution onto the AgNW mesh. The film had a transmittance of 80% in the visible range with a sheet resistance of $12 \Omega \text{ sq}^{-1}$, while the OLEDs exhibited a good efficiency of 19 cd A^{-1} at a current density of 40 mA m^{-2} . Two years later, the same group reported excellent OLEDs with a smooth substrate created by combining SF with a photopolymer.^[169] They deposited a photopolymer, NOA63 (Norland Products, Inc., New Jersey, USA), to form the film (with root mean square roughness of 0.682 nm) on a silk substrate

by spin-coating, which increased the overall smoothness and retained the flexibility and transparency of the substrate. The OLEDs had a remarkable efficiency of 377 cd A^{-1} and an L_{max} of $45\,545 \text{ cd m}^{-2}$, and these numbers were similar to those of the glass-based devices.

In 2017, an ITO-free OLED with eumelanin pigment incorporated into commercial PEDOT:PSS was reported by Pezzella et al.^[170] Focused on overcoming the drawbacks of PEDOT:PSS, including instability in water, low adhesion to organic substrates, and low conductivity compared with those of ITO, they obtained eumelanin-PEDOT:PSS by adding PEDOT:PSS to water with a small amount of dimethyl sulfoxide (DMSO) into isopropyl-dissolved alcohol eumelanin. The film was then fabricated by filtering and spin-coating the blend onto glass, followed by heating to remove the water. The thin film exhibited a high optical transparency greater than 80% in visible light and a conductivity of 370 S cm^{-1} .

Carbon-based materials, such as CNTs and graphene, with their low-cost and good transparency are typically combined with conductive materials to prepare flexible electrodes. Previously reported carbon-based electrodes include laminated electrodes, such as AgNW/graphene,^[171] Al/MWCNTs/Al,^[172] and graphene/Ag thin film,^[173] as well as hybrid compound electrodes, such as PEDOT:PSS/single-walled CNTs (SWCNTs)^[174] and AgNW/SWCNTs.^[175] As electrodes, the compound film exhibits superior optoelectronic characteristics. With the development of materials and fabrication techniques, the roughness and conductivity of carbon-based flexible electrodes can be improved for better performance in the future.

Cytochrome c, a common protein with low molecular weight and an electron carrier in living systems, was first reported as an emitter for OLEDs in 2005.^[176] However, these devices were not stable and exhibited a low external quantum efficiency (EQE) of only $6\text{--}8 \times 10^{-8}\%$ at 13 V. Later, the same researchers enlarged the protein scope, including myoglobin, hemin, and vitamin B12.^[177] The electroluminescence spectra and EQE of myoglobin- and vitamin B12-based devices were similar to the devices based on cytochrome c. Hemin-based devices exhibited a broad spectra with defined peaks at 550, 580, and 800 nm under applied voltages of less than 4.5 V. In addition to these natural emitters, there have been some OLEDs based on biodegradable derivatives and hybrid emitters. Similar to previous research conducted with hybrid LEDs, Richter et al. utilized the bovine submaxillary mucin (BSM) protein as both the binder and stabilizer for hydrophobic nanomaterials in devices.^[178,179] The BSM prevented the aggregation of hydrophobic luminescent polymers, which was a critical issue in multi-layer LEDs.^[178] By including BSM, the electroluminescence of devices changed from merely yellowish-green (BSM-free) to the whole visible range. Recently, Hernandez-Sosa et al. reported the use of riboflavin-tetra butyrate (RFLT), a derivative of vitamin B2, and biodegradability was retained with an improved solubility and less aggregation, and orange-emitting OLEDs were obtained.^[166] These devices exhibited a high turn-on voltage of 11 V, L_{max} of 10 cd m^{-2} , and current efficiency of 0.02 cd A^{-1} , as shown in Figure 8-iii.

Cytochrome c and DNA can also function as an injection layer in OLEDs. Mizutani et al. used a micro-contact printing technique to implement BSA, cytochrome c, and BSA-fluorescein

isothiocyanate as the charge injection and transport layers in OLEDs.^[180] The device with a cytochrome c layer yielded an L_{max} of 100 cd m^{-2} , which was nearly the same as other protein-based OLEDs, as well as an efficiency of 0.02 cd A^{-1} , which was 40 times higher than that of the device without cytochrome c. The first report on DNA-based OLEDs was published by Kobayashi et al. in 2001.^[181] Later, they applied salmon DNA, a by-product from the salmon industry that can easily be transformed into DNA-cetyltrimethylammonium (DNA-CTMA), as an electron transporter in OLEDs.^[182] With good solubility in common organic solvents that enabled solution-processability, DNA-CTMA was widely studied for its use in functional layers throughout the next decade.^[183–185] In 2011, Nguyen et al. fabricated a poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV, electroluminescent layer)-based device with pure DNA as the interlayer and achieved a luminance of 5700 cd m^{-2} and a current efficacy of 0.80 cd A^{-1} , which were significantly higher than that of the device without a DNA layer.^[186] In 2014, Gomez et al. applied the adenine (A) and thymine (T) nucleobases of DNA into OLEDs.^[167] Because of their powder forms and low molecular weights, A and T have helped simplify treatment processes and allowed for the preparation of thin films via molecular beam deposition under high vacuum. The device with T as the electron blocking/hole-transport material exhibited an efficiency of 76 cd A^{-1} and an L_{max} of $132\,000 \text{ cd m}^{-2}$ (Figure 8-iv). One year later, this group evaluated the performance of OLEDs with layers of various components of DNA, specifically the nucleobases of A, T, cytosine (C), guanine (G), and uracil (U).^[187] They found that the two pyrimidines, T and U, were the most thermally unstable, and the relative dielectric constants ranged from 4.0 (G) to 1.6 (U) measured at 1 MHz with a trend of $G < A < C < T < U$. A-based OLEDs exhibited the best performance with a current efficiency of 52 cd A^{-1} and an EQE of 14.3%. **Table 2** summarizes the representative results of the OLEDs containing biodegradable materials.

LECs: LECs are structured so that in between two electrodes, an emitter is combined with an ionic species to form an in situ p-i-n junction. This principle simplifies the fabrication conditions compared with those of OLEDs, enabling fabrication through roll-to-roll printing. Similar to OLEDs, LECs are also considered promising and cost-effective white light-emitting sources.

Recently, biodegradable LECs have attracted significant attention. In some instances, biodegradable ionic polyelectrolytes were used in LECs. Hernandez-Sosa et al. used biodegradable PCL as the ion-solvating polymer in solution-processed LECs.^[154] The active layer, consisting of a blend of super yellow (SY):PCL:tetrabutyl ammonium tetrafluoroborate (TBABF₄), was spin-coated from anisole solution onto substrates. They found that PCL not only exhibited good miscibility with the emitter, but it also exhibited outstanding ion-solvating capability. The devices they prepared demonstrated lifetimes of 30 h, operating at a current density greater than 150 cd m^{-2} . Later this group applied PLGA as the ionic species in the active layer of LECs.^[152] PLGA has an electrochemical window stability ranging from $-2.6\text{--}2 \text{ V}$, which was constant with the variation in the molecular ratio of lactic and glycolic monomers. The solution used for spin-coating to form the active layer was prepared by first dissolving PLGA, SY, and TBABF₄ in anisole separately, followed by mixing the desired ratio. By applying different batches

Table 2. Selected representative results of organic light-emitting diodes (OLEDs) containing biodegradable materials.

Biodegradable materials	Functional layer	Device structures	Turn-on voltage [V]	$L_{\max}$ [cd m^{-2}] (V)	Efficiency [cd A^{-1}] (luminance)	Ref.
BC nanofibers	Substrate	BC/SiO ₂ /ITO/Alq ₃	6	1200	—	[142]
Nanofibrillated cellulose	Substrate	Cellulose/CNT/MoO ₃ /PEDOT:PSS/green polyfluorene/Ca/Al	5	—	—	[145]
CNC	Substrate	CNC on glass/MoO ₃ /Au/ α -NPD/LiF/Al	3.5	74 600	53.7(100)	[143]
Chitin nanofibrils (ChNF)	Substrate	ChNF/ZnS:Ag:MoO ₃ /NPB/Alq ₃ /LiQ:Al	2.5	3890	5	[18]
AgNW/SF	Substrate	AgNW/SF/MoO ₃ /TAPC/CBP:Ir(ppy) ₃ (10 wt%)/TPBi/LiQ:Al	—	19 000	—	[168]
Eumelanin-PEDOT:PSS (Eu-PH)	Electrode	Eu-PH/ α -NPD/Alq ₃ /Ca/Al	6	300(12)	1.8	[170]
Cytochrome c	Emitting layer	ITO/cytochrome c/Al	7	—	—	[188]
RFLT	Emitting layer	ITO/PEDOT:PSS/PVK/RFLT/Al	11	10	0.02(10)	[166]
Vitamin B12	Emitting layer	ITO/Vitamin B12/Al	—	—	—	[177]
BSM	Emitting layer	ITO/BSM-RGB with MWNT/Al–Au	—	—	—	[179]
BSA	Submonolayer	ITO/PEDOT:PSS/BSA/NPB/Alq ₃ /Mg/Al	3.5	20(5)	0.02	[180]
Cytochrome c	Submonolayer	ITO/PEDOT:PSS/cytochrome C/NPB/Alq ₃ /Mg/Al	3	20(5)	1	[180]
DNA-CTMA	Hole-transporting/ electron-blocking layer	ITO/PEDOT-DNA-CTMA (20 nm)/PFO:MEH-PPV/Cs ₂ CO ₃ /Al	6.2	4900	6.3	[185]
DNA	Hole-blocking layer	ITO/PEDOT:PSS/MEH-PPV/DNA-CTMA/Al	2.3	5700	0.8	[186]
A	Hole-transporting/ electron-blocking layer	ITO/PEDOT:PSS/A/CBP:Ir(ppy) ₃ /BCP: Alq ₃ /LiF/Al	5	82 289	51.8	[187]
G	Hole-transporting/ electron-blocking layer	ITO/PEDOT:PSS/G/CBP:Ir(ppy) ₃ /BCP: Alq ₃ /LiF/Al	4.75	17 191	44.3	[187]

BC, bacterial-derived cellulose; Alq₃, tris(8-hydroxyquinolino)aluminum; CNC, cellulose nanocrystal; α -NPD, *N,N'*-di(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine; NPB, *N,N'*-bis(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine; SF, silk fibroin; TAPC, 1,1-bis(4-bis(4-tolyl)-aminophenyl)cyclohexene; RFLT, riboflavin-tetra butyrate; bovine submaxillary mucin; BSA, bovine serum albumin; CTMA, cetyltrimethylammonium; MEH-PPV, poly[2-methoxy-5(2'-ethyl-hexyloxy)-1,4-phenylene vinylene; TPBi, 2,2',2''-(1,3,5-benzenetriyl)tris[1-phenyl-1H-benzimidazole]; CBP, 4,4'-bis(N-carbazolyl)-2,2'-biphenyl; Ir(ppy)₃, tris[2-phenylpyridinato-C₂N]iridium(III); PFO, poly(9,9-dioctylfluorene-2,7-diyl); BCP, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; A, adenine; G, guanine.

of PLGA synthesized with lactic:glycolic monomer ratios of 85:15, 75:25, and 65:35, the device performance indicated that the addition of PLGA could reduce the turn-on voltage from 7 V (obtained by the device without PLGA) to 4.7, 4.3, and 4.1 V, respectively. The devices with a turn-on voltage of 4.1 V were best-performing with an $L_{\max}$ of 3800 cd m^{-2} . Recently, this group applied a nonhalogenated biodegradable solid polymer electrolyte based on poly(ϵ -caprolactone-co-trimethylene carbonate) (PCL-co-TMC) and tetrabutylammonium bis-oxalato borate (TBABOB) to LECs, and the solution-processable devices exhibited a current efficiency of 2 cd A^{-1} and a luminance greater than 12 000 cd m^{-2} .^[146] Additionally, they used an inkjet printing technique to fabricate LECs on flexible and biodegradable cellulose-based substrates. The devices showed compatible lifetimes with transient applications. These cases demonstrated that the design of new components in LECs using biodegradable materials could be an effective strategy in enhancing the performance of devices, as shown in **Figure 9**.

2.4. Other Electronic Devices

In addition to solar cells, OFETs, and LEDs, there are other devices (e.g., batteries, sensors, drug delivery devices, and

implantable devices) that would greatly benefit from the use of biodegradable materials.^[189–193] A power source is one of the most important components in regard to biodegradable electronic devices; however, a fully biodegradable power source has proven to be a major challenge in the application of such devices (e.g., self-powered diagnostic and therapeutic implants). Yin et al. reported a high-performance, biodegradable battery as an in vivo on-board power supply. In their work, they used a dissolvable Mg anode, which possessed a high theoretical energy density and excellent biocompatibility. Meanwhile, MoO₃ (1 g L⁻¹ in aqueous solution) served as the cathode material, and alginate hydrogel functioned as the electrolyte. Significantly, after coating with polyanhydride/PLGA, the biodegradable batteries demonstrated a lifetime of 12 days. Moreover, a single Mg-MoO₃ cell was able to provide sufficient power for an LED, a calculator, and a signal detector, demonstrating its feasibility in ultralow-power implantable devices, while simultaneously maintaining strong functions. Furthermore, in vivo experiments demonstrated that the battery could fully degrade after 4 weeks of implantation using the Sprague-Dawley rat model, as shown in **Figure 10-i**.^[194] Moreover, a fully biodegradable/bioresorbable capacitor was also proposed for energy storage unit in an implantable device.^[195] The capacitor includes PLA supporting substrate, PLA nanopillar arrays, self-assembled

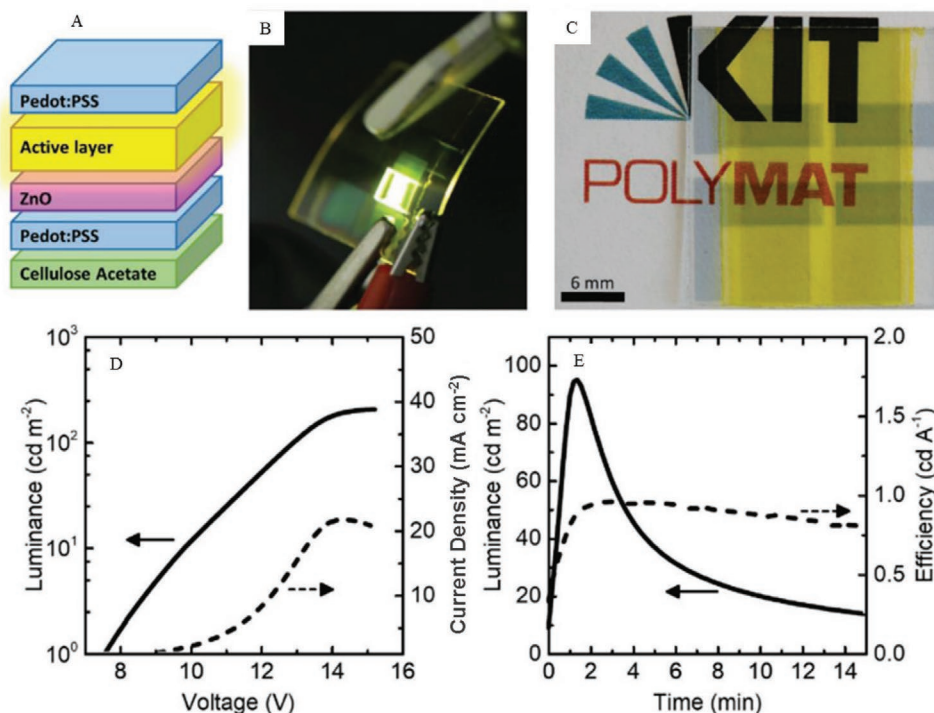


Figure 9. A) Architecture of fully-printed device. B) Photograph of fully-printed device under operation with active layer of 1:0.1:0.075 (SY: PCL-co-TMC (80:20): TBABOB) (SY: super yellow; PCL-co-TMC: poly(ϵ -caprolactone-co-trimethylene carbonate); TBABOB: tetrabutylammonium bis-oxalato borate). C) Photograph of complete device in top view. D,E) Device performance. Reproduced with permission.^[146] Copyright 2018, Wiley-VCH.

zinc oxide nanoporous layer, PVA/PBS hydrogel, and Fe film (Figure 10-ii(A)). Long-term normal work time was reached up to 30 days in PBS and 50 days in Sprague-Dawley rat. Significantly, the capacitor can be fully degraded after immersing into PBS for 4 months in the in vitro experiment, and 5 months in the in vivo experiment (Figure 10-ii(B,C)). Further, for the longer life-time implants (such as powering pacemakers), biodegradable self-powered monocrystalline silicon photovoltaics meet the requirement and can be the choice, through implanting the device under 4 mm of porcine skin and fat to utilize near-infrared illumination.^[196] Therefore, the reported biodegradable power source devices, which possess excellent power output performance with different normal work time and fully degradable time, offer a choice for the design of implantable devices with specific life-time.

Blood flow monitors are crucial in clinical medicine and need biodegradable, implantable, and wireless sensors for accurate detection. Recently, Bao et al. designed an arterial-pulse sensor for vessel anastomoses monitoring to avoid surgery for extraction of the implant. Of great importance, the sensor was wireless and used a well-established radio-frequency coupling method. Additionally, it was made entirely of biodegradable materials that could be resorbed after several months, thus eliminating the need for device removal. In this work, the device was fabricated by laminating the Mg electrical interconnect with the PGS dielectric layer for the pressure sensitive regions. The poly(octamethylene maleate (anhydride) citrate), polyhydroxybutyrate/polyhydroxyvalerate (PHB/PHV) packaging layers, and PLA spacer were used for the bilayer coils, which were then combined with a LCR resonator circuit to

construct wireless sensor.^[197] After being implanted into a rat model, the device showed good sensitivity for blood flow. The sensor was partially degraded after 12 weeks with only PHB/PHV remaining. In addition to blood flow monitors, various types of diagnostic and therapeutic implantable devices can also be used for clinical medicine, which highly demand biodegradability and bioresorbability as well to avoid the unnecessary of additional secondary surgery.^[198] For instance, biodegradable/bioresorbable temperature sensors,^[199] pH sensors,^[200] and electrophysiological sensors^[190] can be used for real-time monitoring of tissues or organs after primary surgery. Moreover, biodegradable/bioresorbable actuators can be used for surgical site therapy and accurate drug delivery based on the feedback signal from biodegradable/bioresorbable sensors.^[201] Typically, a wirelessly controlled therapeutic actuator was developed with biodegradable structure of silk substrate/Mg serpentine resistor and power-receiving coil/silk overcoat. Such actuator can serve as thermal heater to combat infection in the surgical site, as well as drug delivery system with controllable drug release kinetics (Figure 11). Commonly, Mg is an important component as electrode or functional part in a transient device, which shows great potential to construct fully biodegradable device by combining with natural biodegradable substrate. Significantly, integration of biodegradable/bioresorbable sensors and actuators with circuit to construct fully biodegradable implants will be meaningful for future clinical medicine.

The above biodegradable electronics are mainly implantable devices for clinical medicine. Actually, there are many types of biodegradable electronic devices beyond implantable devices. Hu et al. demonstrated a novel all-wood-structured

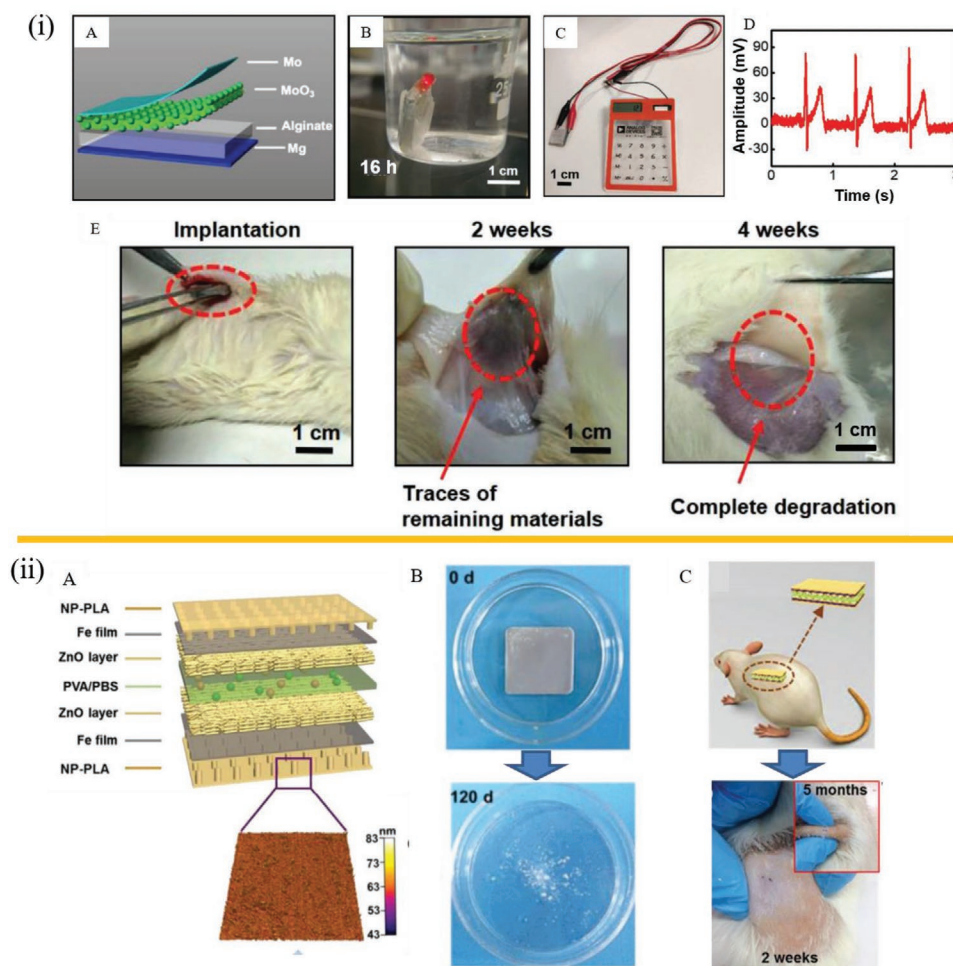


Figure 10. i) A: Schematic illustration of battery structure. B–D: Light-emitting diode, calculator, and electrocardiogram powered by battery. E: In vivo degradation evaluation of battery in subcutaneous area of Sprague-Dawley rats upon implantation and after 2 and 4 weeks. Reproduced with permission.^[194] Copyright 2018, Wiley-VCH. ii) A: Structure schematic of biodegradable capacitor. B,C: Full degradation in PBS with in vitro experiment and in Sprague-Dawley rat with in vivo experiment. Reproduced with permission.^[195] Copyright 2019, Wiley-VCH.

biodegradable supercapacitor, including activated wood carbon anode, thin wood membrane separator, and MnO₂/wood carbon cathode (Figure 12-i).^[202] Owing to the porous and biodegradable nature of carbonized wood, the proposed supercapacitor exhibited a high areal capacitance and a high energy/power density, and can be biodegraded in the nature. Biodegradable strain gauges were constructed by evaporation-condensation-mediated laser printing and sintering of biodegradable Zn nanoparticles onto sodium carboxymethylcellulose bioresorbable substrate (Figure 12-ii), showing high sensitivity subjected to stretch or deflection.^[203] Zhou et al. demonstrated a biodegradable and recyclable antenna.^[204] Transient circuits were first constructed by combining room-temperature liquid metals (RTLTM) as the electronic circuit and water-soluble PVA as the packaging material. Subsequently, the surface patterning and packaging of RTLTM can be applied as a transient antenna for a passive near-field communication (NFC) tag, showing good communication between NFC tag and cell phone (Figure 12-iii). Moreover, Hu et al. reported biodegradable transient lithium-ion battery, including a trilayer anode with integrated structure, a high-

capacity origami cathode with high mass loading, and a bilayer battery packaging (Figure 12-iv).^[205] Significantly, all components can be dissolved into alkali solution. Therefore, based on the above-listed electronic devices, integrating synthesized biodegradable active material/electrode with natural biodegradable substrate is a popular and useful method to construct fully biodegradable electronic devices with high performance.

3. Green Processing for Green Electronics

Device fabrication by means of green processing is as important as the use of biodegradable materials in green electronics, and it includes the use of non-toxic solvents, eco-friendly functional layers, and large-scale, low-cost fabrication methods. Essentially, green processing can effectively suppress the emission of toxic substances into the environment during device fabrication. Simultaneously, high-performance devices created through green processing are also needed, especially when compared with conventional methods. Therefore, balancing

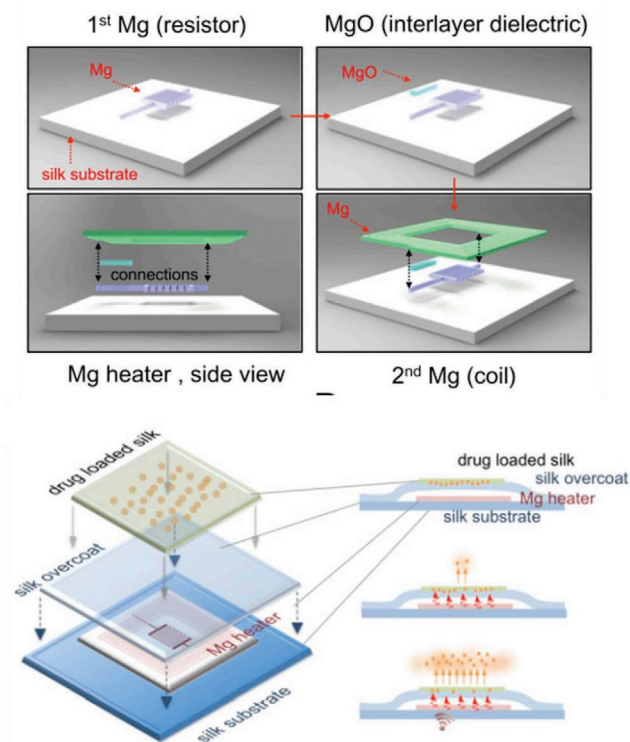


Figure 11. Schematic structure of the wirelessly controlled therapeutic actuator with thermal heating and drug delivery functions. Reproduced with permission.^[20] Copyright 2014, National Academy of Sciences.

green processing with device performance is the key for successful green fabrication. The following sections will provide an overview regarding the green processing applied during device fabrication and illuminate the feasibility of green processing for high-performance electronics such as solar cells, OFETs, LEDs, and other devices.

3.1. Green Processing of Solar Cells

High-performance photovoltaics are being pursued by photovoltaic researchers. Notably, emerging photovoltaics, especially solution-processed PSCs and OPVs,^[67,206,207] are expected to be commercialized and may account for a great percentage of the international photovoltaics market. However, green processing is highly desired in device fabrication, owing to the intrinsic toxicity of the components and solvents used in photovoltaics. Based on the green concept, this section reviews recent reports regarding green processing in the fabrication of PSCs and OPVs.

3.1.1. Green Processing of PSCs

Solution processing with one-step spin-coating is one of the most effective methods for the fabrication of high-quality perovskite film on a laboratory scale. Unfortunately, these highly efficient PSCs are fabricated through the utilization of high boiling point and polar or halogenated toxic solvents for the ETL, HTL,

and perovskite layer, which are extremely harmful to both the environment and human health, even though they are beneficial in producing high-quality film. Moreover, environmentally friendly Pb-free perovskite is highly desired, owing to the toxicity that currently exists in conventional perovskite with lead ions. In fact, tin (Sn), Ge, bismuth (Bi), and stibium (Sb) ions are considered as alternative ions for the fabrication of environmentally friendly PSCs.^[208–211] Furthermore, scalable fabrication techniques with less raw material waste are also being sought for the commercialization of PSCs. Therefore, we will summarize the progress of recent research based on the green processing concept for PSCs.

Green Solvents for PSCs: Significantly, the solvent is an important factor in creating high-quality film for the ETL, HTL, and perovskite layer. Commonly, the solvents used throughout the entire fabrication process of PSCs include toxic *N,N*-dimethylformamide (DMF),^[212] DMSO,^[213] dimethylacetamide,^[214] and *N*-methyl-2-pyrrolidone (NMP)^[215] in the precursor solution, while chlorobenzene (CB),^[216,217,218] toluene (TLN),^[219] and diethylether^[220] are used as the antisolvents during spin-coating or as solvents to dissolve the electron/hole-transport materials.

Recently, non-hazardous and low-toxicity solvent systems were used as alternatives to conventional toxic solvents in a perovskite precursor solution, and smooth pinhole-free perovskite films were obtained. Inspired by the “healing” process with methylamine (MA) gas in a post-fabrication strategy,^[221] Snaith et al. bubbled MA gas into its low boiling point with highly polar and aprotic acetonitrile (ACN) to form an industrially scaled ACN/MA green solvent system, which could enhance the dissolution of $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor salts.^[222] The proposed method was significantly beneficial in forming ultrasMOOTH pinhole-free perovskite film on substrate areas as large as 125 cm^2 , which was comparable to the film prepared by the DMF solvent method, owing to the rapid crystallization of the perovskite at room temperature in an ACN/MA solvent system. The morphology of the crystalline film and mirror-like 125 cm^2 perovskite on substrate processed from the ACN/MA solvent system are shown in **Figure 13-i**. The obtained high-quality perovskite films allowed for a device efficiency of 19% for 0.09 cm^2 and greater than 15% for 0.7 cm^2 . A non-hazardous solvent system is also necessary for the solution-processing of PSCs, which is important in terms of occupational safety in industrial manufacturing. Tait et al. used the Hansen solubility parameters (HSP) as guidelines and determined a solvent mixture miscible with perovskite precursors ($\text{CH}_3\text{NH}_3\text{I}$, PbAc_2 , and PbCl_2).^[223] A non-hazardous solvent system, γ -butyrolactone/ethanol/acetic acid (60/20/20 vol%), was chosen to fabricate a pinhole-free perovskite film. The best performance obtained was 14.5% for 0.13 cm^2 , which was equivalent to the reference DMF-based PSCs. Moreover, the non-hazardous solvent system was used as perovskite ink to implement blade-coating, and the blade-coated 4 cm^2 solar modules showed an efficiency of 11.9% with impressive pinhole-free perovskite film. Water was considered the ideal green solvent; however, its solubility was limited by lead halide and organic methylammonium iodide (MAI) or formamidinium iodide (FAI). Triggered by the environmentally friendly concept, Song et al. introduced aqueous $\text{Pb}(\text{NO}_3)_2$ into a two-step spin-coating process to fabricate a perovskite active layer.^[224] The aqueous $\text{Pb}(\text{NO}_3)_2$ and MAI in isopropanol were

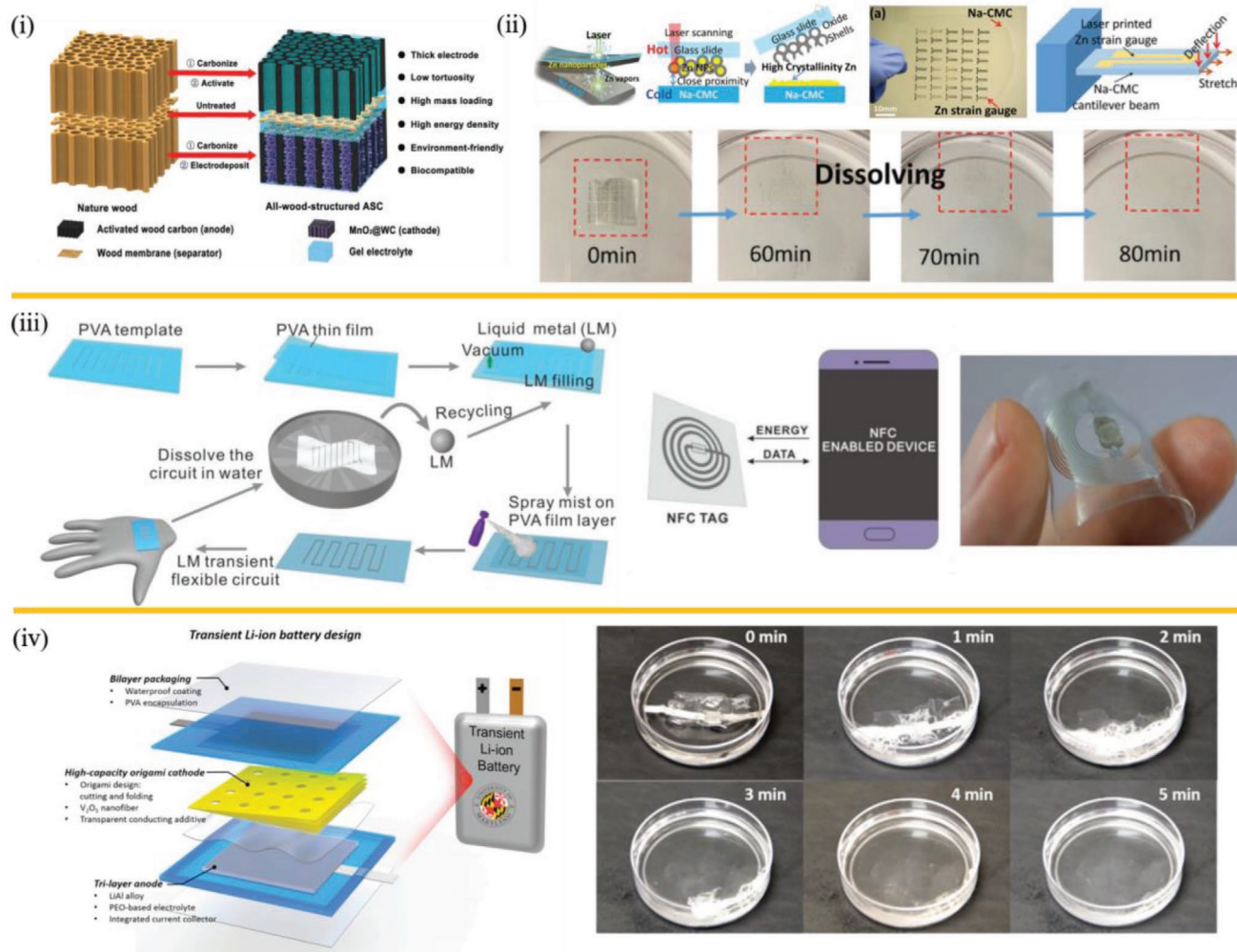


Figure 12. i) Schematic illustration of the construction of all-wood-structured supercapacitor. Reproduced with permission.^[202] Copyright 2017, Royal Society of Chemistry. ii) Schematics of biodegradable strain gauges constructed by laser printing process and dissolving test in distilled water. Reproduced with permission.^[203] Copyright 2017, Wiley-VCH. iii) Liquid metal transient circuit fabrication process and biodegradable antenna. Reproduced with permission.^[204] Copyright 2019, Wiley-VCH. iv) Schematic of transient Li-ion battery demonstration and degradation test in 1.5 M KOH aqueous solution. Reproduced with permission.^[205] Copyright 2016, Wiley-VCH.

successively spin-coated on mesoporous TiO_2 film. A relatively high coverage of perovskite was observed, and the best PSC performance was 13.7%. Although the efficiency of this approach was lower than conventional processing with a toxic solvent, the water system indicated great potential to replace toxic solvents and speed up industrial-scale commercialization. Owing to the limited solubility of perovskite precursors in polar solvent (except DMSO and DMF) and polar nature of green solvents, the selectable green solvents for perovskite precursor dissolution are limited. Furthermore, it is still difficult to balance the solubility and film quality with singular green solvent. Mixture green solvents (non-halogenated and non-aromatic solvents, esters, alcohols, and water) with HSP as guidelines show great potential to dissolve perovskite precursors and form perovskite film with high quality, which can be the guidance for green solvent selection.

Besides the precursor solution, an antisolvent step has been commonly utilized in one-step spin-coating fabrication to facili-

tate crystallization and achieve high-performance PSCs. However, the widely used antisolvents have high toxicity and further hinder large-scale manufacturing. Recently, anisole (with its relative non-toxicity, high boiling point, and frequent use in cosmetics and food)^[227] was proposed as an environmentally friendly antisolvent that could be induced to obtain high-quality perovskite film. The best efficiency attained with the anisole antisolvent step approached 20%, which was on par with the toxic CB and TLN antisolvent process, and it indicated great potential as a green solvent for the fabrication of PSCs. Zhang et al. fabricated planar PSCs by using anisole as a green antisolvent and obtained smooth surfaces, large grains, and a low defect density, resulting in a superior efficiency of 19.42%, which was comparable to the toxic CB antisolvent process.^[228] To further investigate the influence of anisole antisolvent on the process window, Jung et al. prepared perovskite thin film using one-step spin-coating with anisole, CB, TLN, and other antisolvents.^[229] The comparison was made under different

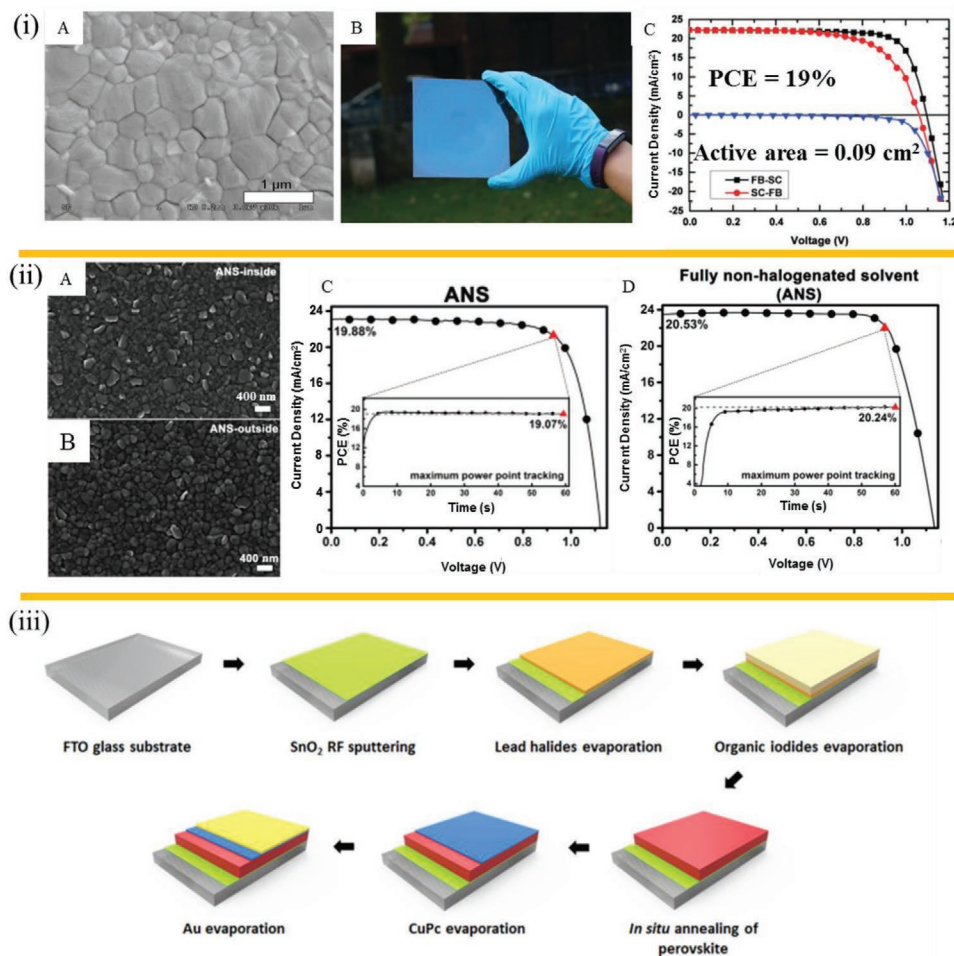


Figure 13. i) A,B: Morphology and mirror-like perovskite film prepared from acetonitrile/ methylamine (ACN/MA) green solvent system. C: Current-voltage (J - V) curves from obtained perovskite solar cell (PSC) with active area of 0.09 cm². Reproduced with permission.^[222] Copyright 2017, Royal Society of Chemistry. ii) A,B: Scanning electron microscope (SEM) images of perovskite using anisole as antisolvent both inside and outside glovebox. C: J - V curve of PSC with anisole as antisolvent. D: J - V curve of PSC with anisole as antisolvent and solvent for hole-transporting materials. Reproduced with permission.^[225] Copyright 2018, Wiley-VCH. iii) Schematic illustration of fabrication procedure of all-vacuum-deposition method. Reproduced with permission.^[226] Copyright 2019, Wiley-VCH.

process conditions such as the DMF/DMSO ratio, antisolvent dripping times, and antisolvent dripping volumes. Significantly, the anisole antisolvent method exhibited an ultrawide process window for perovskite thin film fabrication. The best efficiencies were 19.76% and 17.39% for devices with a small (0.14 cm²) and large (1.08 cm²) active area, respectively. Accordingly, the superiority of anisole is due to its unique physicochemical properties (e.g., high boiling point and viscosity) and H-bonding with DMF/DMSO to form excessive nucleation. This green antisolvent with an ultrawide process window opened a pathway for the industrialization of environmentally friendly PSCs, as well as releasing experimenters from the skillful handling of spin coating tricks. Furthermore, Saliba et al. applied the greener and nonhalogenated anisole as antisolvent to fabricate devices both inside and outside a glovebox and demonstrated efficiencies of 19.9% and 15.5%, respectively.^[225] Specifically, the green processing fabrication that occurred outside the glovebox was meaningful in terms of large-scale industrialization, as it could definitely simplify the fabrication of devices while reducing

systematic health risks. They also fabricated the device with anisole as both the antisolvent and solvent for hole-transporting materials (HTM), and the unprecedented efficiency was close to 20.5% (Figure 13-ii). This was the best recorded efficiency using anisole for wholly green non-halogenated solvent processing, and it demonstrated the excellent potential of anisole in the green processing fabrication of PSCs. Furthermore, this green anisole antisolvent processing technique was also used for flexible PSCs and attained an efficiency over 17% with excellent stability under different bending radii. Based on the above discussion, anisole-based antisolvent processing seems an alternative green processing. However, anisole is still classified as aromatic-contained solvents though with low/non-toxicity. Actually, antisolvent-free processing is expected in the future industrial manufacture, which needs to deeply study the crystallization kinetics of perovskite in green solvents to realize high quality film without antisolvent step. Additionally, ethyl acetate, *o*-xylene (*o*-XY), and 1,2,4-trimethylbenzene (TMB) were recently reported as low-toxic non-halogenated antisolvents

and/or solvents that could dissolve the ETL/HTL.^[230,231] Therefore, realizing fully green solvents in the fabrication of PSCs is possible through HSP and crystallization kinetics as guidelines.

In practice, vapor deposition is an effective method to avoid the use of toxic solvents, although it incurs high production costs. Most recently, Fan et al. developed the all-vacuum-deposition process to fabricate planar PSCs, including the sputtering of SnO₂ ETL at room temperature, vapor deposition of lead halides and organic iodides, and thermal evaporation of CuPc, HTL, and Au electrodes, as illustrated in Figure 13-iii.^[226] The whole fabrication procedure, which totally avoided the use of solvents, improved the perovskite film quality. Consequently, the top-performing device, based on MA_{0.56}FA_{0.44}PbI_{2.67}Br_{0.33}, delivered a PCE of 15.14% with a V_{oc} of 1.02 V, J_{sc} of 19.16 mA cm⁻², and an FF of 77.3%. Xie et al. also applied a fully green vapor deposition to fabricate stable and scalable 3D–2D planar PSCs. Owing to the stabilized effect of 2D perovskite, the obtained efficiency was 16.5%. Significantly, the unencapsulated devices retained 81% and 74% of the initial efficiency after 30 days under 55% humidity and heating at 80 °C, thereby demonstrating the great commercial potential of fully green vapor deposition in the fabrication of PSCs.^[232] To avoid the large energy consumption of vacuum-deposition, a solvent- and vacuum-free route was proposed by Han et al.^[233] In their innovative method, CH₃NH₂I or PbI₂ powder was blown with dried CH₃NH₂ gas to form CH₃NH₂I·3CH₃NH₂ (liquid) and PbI₂·CH₃NH₂ (paste). Then, the liquid CH₃NH₂I·3CH₃NH₂ and paste PbI₂·CH₃NH₂ were blended stoichiometrically, aiming for the rapid conversion of amine complex precursors to perovskite films, followed by a pressure application step. The solvent- and vacuum-free route reached a certified PCE of 12.1% in 36 cm² PSC modules. Importantly, this method offers a chance for the fully green processing of non-toxic solvent or solvent-free, heavy metal-free, and low energy consumption in future PSC industry.

Lead-Free PSCs: At present, the highest efficiencies of PSCs are all from Pb-based hybrid perovskite,^[234] owing to the significant role of the Pb²⁺ ion with a lone pair of electrons (6s²) in the determination of the perovskite electronic structure.^[234] However, the intrinsic toxicity of the lead ion in perovskite causes concerns regarding its environmental friendliness, which may hinder the speed of its commercialization. Although there is less than 1 g m⁻² of metal in a solar panel, perovskite tends to be dissolved or degraded into harmful compounds with heavy metal under appropriate external conditions, which may leach into the surrounding environment and be ingested by a human body through gastrointestinal, respiratory, and/or dermal uptake.^[236] Therefore, it is desirable to uncover alternatives to fabricate Pb-free PSCs. As mentioned above, a variety of potential materials can be used for low-toxic Pb-free perovskite. Among them, Sn is being widely explored as a substitute for Pb, and in recent reports, it is holding a record efficiency of 9.6% among all Pb-free PSCs.^[208] Other perovskites, such as those based on Bi and Sb, are stable in air but exhibit poor solar cell performance.^[237,238]

Sn is in the same periodic group as Pb and exhibits properties similar to Pb, thereby attracting great interest as a potential alternative.^[239] Common Sn-based perovskites are methylammonium tin iodide (MASnI₃), formamidinium tin iodide

(FASnI₃), and cesium tin iodide (CsSnI₃) with direct bandgaps of 1.20, 1.41, and 1.30 eV, respectively.^[240] These bandgaps are narrower than those of the Pb-based perovskites, endowing them with an extended absorption spectra to 1000 nm.^[241] However, Sn²⁺ is easily oxidized to Sn⁴⁺, which generally induces a low V_{oc} because of its role as a p-type dopant.^[240] To resolve this issue, several methods have been proposed to alleviate and suppress oxidation. Song et al. applied a two-step cation-exchange approach to deposit the MASnI₃ layer with the suppression of Sn²⁺ oxidation. In this work, a hydrazinium tin iodide (N₂H₅SnI₃, HASnI₃) layer was first deposited onto a mesoporous substrate. Then, the HASnI₃ film was transformed in situ into MASnI₃ in a methylamine atmosphere. The obtained efficiency approached 7.13% with good reproducibility, as shown in Figure 14-i.^[242] Fan et al. achieved a record stability of FASnI₃ with only 20% degradation in the PCE for the encapsulated device exposed to air for more than 500 h. The introduced hydroxybenzene sulfonic acid and/or its salt played a significant role in effectively passivating the grain surface and suppressing the oxidation of Sn²⁺ (Figure 14-ii).^[243] Moreover, Islam et al. applied 5-ammonium valeric acid iodide (5-AVAI) as an additive to the perovskite that could form H-bonds with I⁻ present in the SnI₆⁴⁻ octahedron to promote the crystal growth of the perovskite, thereby resulting in a pinhole-free, homogeneous, and stable FASnI₃ solar cell with an efficiency of 7% (Figure 14-iii).^[244] Despite low toxicity of Sn-based perovskites, the poor stability due to the easy oxidation of Sn²⁺ and the severe recombination make them difficult to replace Pb-based perovskites. Accordingly, additives included in the perovskite precursor appeared to be an effective way to suppress the oxidation of Sn²⁺ to Sn⁴⁺ and achieve enhanced PSC performance.

Ge was proven to be another alternative for Pb-free perovskite through a theoretical and experimental investigation.^[209] However, Ge-based PSCs exhibited poor device performance when compared to that of Sn- and Pb-based PSCs, most likely because of its high oxidation tendency and poor film morphology.^[245] Adjusting the B-site to form mixed Sn-Ge perovskite could be a promising approach to enhance PSC performance. FA_{0.75}MA_{0.25}Sn_{0.95}Ge_{0.05}I₃ with an ideal bandgap of 1.4–1.5 eV was obtained, and the efficiency increased to 4.48% when measured in air without encapsulation. Interestingly, after 72 h in a dark atmosphere containing nitrogen, the same device displayed an increased efficiency to 6.90%, owing to the increments in J_{sc} and FF.^[246] CsSn_{0.5}Ge_{0.5}I₃ perovskite realized native-oxide passivation, which allowed the resultant device to exhibit a quite stable performance and a drop of less than 10% in the PCE upon continuous work for 500 h in a glovebox under 1-sun illumination.^[247]

Bi- and Sb-based perovskites are stable in air, and photoactive structures with a chemical formula of A₃M₂I₉ (A: MA, Cs; M: Bi, Sb) are perovskite-like with either a 0D or 2D structure.^[211] However, the highest efficiencies of Bi- and Sb-based PSCs are 3.17% and 2.77%, respectively, which are much lower than those of Sn- and Pb-based PSCs.^[248,249] The low efficiency is ascribed to the poor surface coverage of perovskite film and high exciton binding energies, resulting in low short-circuit current densities and efficiencies.^[245] Therefore, high-quality Bi- and Sb-based perovskite films are desirable to improve Pb-free PSC performance. Table 3 summarizes the performances

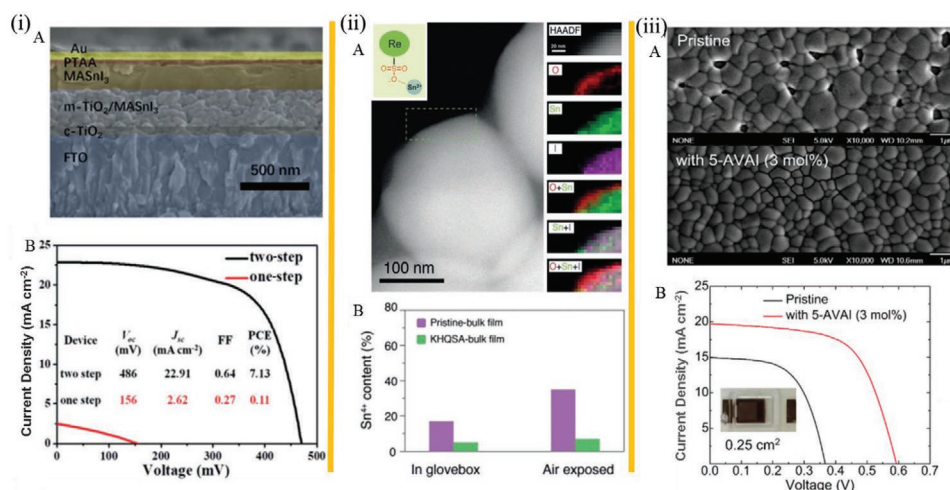


Figure 14. i) A: Device architecture of mesoporous perovskite solar cell (PSC) with two-step MASnI₃ deposition. B: Current–voltage (*J*–*V*) curves of devices based on one-step or two-step MASnI₃ layer. Reproduced with permission.^[242] Copyright 2019, Wiley-VCH. ii) A: STEM-HAADF image and STEM-EELS maps of FASnI₃ grain boundary with 10% potassium salt of hydroquinone sulfonic acid (KHQSA) modification. B: Sn⁴⁺ content determination in pristine- and KHQSA-bulk film after exposed to air (relative humidity ≈20%) for 10 h or stored in glovebox. Reproduced with permission.^[243] Copyright 2019, Wiley-VCH. iii) A: Scanning electron microscope (SEM) images of pristine and 5-ammonium valeric acid iodide (5-AVAI) added FASnI₃ films. B: *J*–*V* curves of pristine and 5-AVAI added FASnI₃ devices with area of 0.25 cm². Reproduced with permission.^[244] Copyright 2018, American Chemical Society.

of recently reported Pb-free PSCs. Clearly, the relatively low performances do not meet the requirements necessary for commercialization, owing to the non-cubic crystal structure of Bi- and Sb-based perovskite with large bandgap. Most probably, Sn-based perovskite is a promising green material for green processing of solar cells, once solving the problem of Sn²⁺ oxidation and enhancing their efficiency and stability greatly. Nevertheless, great efforts are still necessary to improve the efficiency and stability of Pb-free PSCs.

Recycling of PSCs: Upon closer examination of the device architecture of PSCs, the metal electrode, transparent conductive oxide, and Pb-based perovskite are what impact the environment the most. Encapsulation is an effective way to prevent the leakage of Pb during the working lifetime of a device. However, international e-waste disposal regulations suggest collecting obsolete devices and discarding them immediately.^[268] Moreover, the manufacturing of FTO with compact and mesoporous TiO₂ consumes most of the primary energy of embedded materials and contributes to most of the carbon footprint.^[269] Thus, to fully realize the recovery and/or recycling of valued components is significantly meaningful in terms of the green processing of PSCs.

Docampo et al. applied a solution process to dissolve most of the layers in a PSC device to recycle the PbI₂ and glass/FTO.^[270] For example, the HTM can dissolve in CB; the perovskite can be transformed into MAI and PbI₂, and the MAI can be extracted in water. PbI₂ and TiO₂ can be removed by DMF, and the PbI₂ can be further recovered for recycling, as shown in Figure 15-i. The recycled PbI₂ and glass/FTO can then be used for the fabrication of recycled devices. The efficiency was approximately 15% for devices fabricated with three-time recycling, maintaining the 14.6% efficiency of the fresh devices and sufficiently demonstrating the effectiveness of recycling in this procedure. At the same time, Hagfeldt et al. developed a similar

process to recycle the substrates of mesoporous PSCs. The photovoltaic parameters (V_{oc} , J_{sc} , FF, and PCE) of devices fabricated on recycled substrates were similar compared with those of the original values, as shown in 15-ii.^[271] Moreover, Kim et al. applied a selective mechanism to treat with halide perovskites and recovered a mesoporous-TiO₂-coated FTO substrate (Figure 15-iii).^[272] The device performance remained the same as the initial value of 15% even after recycling had occurred ten times. The recycling of PSCs could reduce energy consumption and fabrication costs.

3.1.2. Green Processing of Organic Photovoltaics

Over the past decades, great efforts were made in the research of OPVs that led to an increased PCE of more than 16%, which meets the threshold value required for industrialization and commercialization.^[273–277] Historically, OPVs were typically fabricated via a simple solution printing technique in a laboratory, and halogenated and/or aromatic solvents were chosen as the processing solvents to meet the requirements of phase separation. Highly π -conjugated structures within the light-harvesting materials can be dissolved according to the “like-dissolves-like” rule. Good dissolution indicates that the light-harvesting materials have good film-forming potential and favorable morphology, which makes a significant difference in exciton diffusion, charge generation, and transport.^[278–281] However, these highly toxic halogenated and aromatic solvents are harmful to the health of humans and the environment, which goes against sustainable development and indicates they are not suitable for the mass production and commercialization of OPV technology.^[282] Therefore, it is urgent that environment-friendly alternatives are found to remove toxic solvents from the OPVs, which achieve efficiencies similar to their halogenated counterparts. In this

Table 3. Summary of recently reported performances of lead-free perovskite solar cells (PSCs).

Device structures	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF [%]	PCE [%]	Ref.
ITO/PEDOT:PSS/GA _{0.2} FA _{0.78} SnI ₃ -1% EDAl ₂ /C ₆₀ /BCP/Ag	21.2	0.619	0.729	9.6	[208]
ITO/PEDOT:PSS/FASnI ₃ /PCBM/BCP/Ag	18.89	0.59	0.62	7.0	[244]
ITO/PEDOT:PSS/FA _{0.75} MA _{0.25} SnI ₃ /C ₆₀ /BCP/Al	24.3	0.55	67.3	9.06	[250]
FTO/c-TiO ₂ /mp-TiO ₂ /MASnI ₃ /PTAA/Au	22.91	0.486	64	7.13	[242]
ITO/NiO _x /FASnI ₃ /PCBM/Ag	17.64	0.552	69.4	6.76	[243]
ITO/PEDOT:PSS/C ₅ FA _{1-x} SnI ₃ /C ₆₀ /BCP/Ag	20.70	0.44	66.8	6.08	[251]
ITO/PEDOT:PSS/FA _{0.75} MA _{0.25} SnI ₃ /C ₆₀ /BCP/Ag	19.4	0.55	0.67	7.2	[252]
ITO/PEDOT:PSS/FA _{0.75} MA _{0.25} SnI ₃ + 10% SnF ₂ /C ₆₀ /BCP/Ag	21.2	0.61	62.7	8.12	[253]
ITO/PEDOT/FASnI ₃ + 10% SnF ₂ + TMA/C ₆₀ : 1 wt% TBAI/Ag	22.45	0.47	67.8	7.09	[254]
ITO/c-TiO ₂ /CsSnI ₃ (quantum rods)/Spiro-OMeTAD/Au	23.2	0.86	65	12.96	[255]
ITO/c-TiO ₂ /CsSnBr ₃ (quantum rods)/Spiro-OMeTAD/Au	21.23	0.85	58	10.46	[255]
ITO/c-TiO ₂ /CsSnCl ₃ (quantum rods)/Spiro-OMeTAD/Au	19.82	0.87	56	9.66	[255]
FTO/c-TiO ₂ /mp-TiO ₂ /[en]FASnI ₃ + 15% SnF ₂ /TPE/Au	22.54	0.46	69.74	7.23	[256]
ITO/LiF/ PEDOT:PSS/(PEA, FA) SnI ₃ /C ₆₀ /BCP/Ag	20.07	0.47	74	6.98	[257]
FTO/c-TiO ₂ /[en]FASnI ₃ + 15% SnF ₂ /PTAA/Au	22.54	0.48	65.96	7.14	[258]
FTO/PCBM/CsSn _{0.5} Ge _{0.5} I ₃ /native oxide/Spiro-OMeTAD/Au	18.61	0.63	60.6	7.11	[247]
FTO/c-TiO ₂ /MAGel ₃ /Spiro-OMeTAD/Au	4.0	0.15	30	0.20	[209]
FTO/c-TiO ₂ /CsGel ₃ /Spiro-OMeTAD/Au	5.7	0.074	27	0.11	[209]
FTO/c-TiO ₂ /mp-TiO ₂ /MA ₃ Bi ₂ I ₉ /Spiro-OMeTAD/Au	1.10	0.653	49.6	0.356	[259]
FTO/c-TiO ₂ /mp-TiO ₂ /MA ₃ Bi ₂ I ₉ /Spiro-OMeTAD/Au	2.95	0.81	69	1.64	[237]
FTO/c-TiO ₂ /mp-TiO ₂ /MA ₃ Bi ₂ I ₉ /P3HT/Au	4.02	1.01	78	3.17	[248]
FTO/c-TiO ₂ /CsBi ₃ I ₁₀ /carbon	4.75	0.46	69.18	1.51	[260]
FTO/c-TiO ₂ /MABi ₃ I ₁₀ /carbon	3.40	0.47	41.44	0.67	[260]
FTO/c-TiO ₂ /FABi ₃ I ₁₀ /carbon	3.88	0.45	49.73	0.87	[260]
FTO/c-TiO ₂ /mp-TiO ₂ /PHABi ₄ /P3HT/Au	6.03	0.58	22	0.78	[261]
FTO/c-TiO ₂ /[AT][Bi ₄]/ZrO ₂ /carbon	3.29	0.37	39	0.47	[262]
FTO/c-TiO ₂ /mp-TiO ₂ /AgBi ₂ I ₇ /P3HT/Au	3.30	0.56	67.41	1.22	[263]
FTO/c-TiO ₂ /CsAgBiBr ₆ /MoO ₃ /Ag	3.82	1.01	65	2.51	[264]
ITO/PEDOT:PSS/perylene/HI-CB-MA ₃ Sb ₂ I ₉ /PC ₇₀ BM/C ₆₀ /BCP/Al	5.98	0.69	59.62	2.46	[249]
FTO/c-TiO ₂ /FA ₃ Sb ₂ I ₉ /Spiro-OMeTAD/Au	1.84	0.66	63	0.76	[238]
FTO/c-TiO ₂ /mp-TiO ₂ /MA ₃ Sb ₂ Cl _{9-x} /Spiro-OMeTAD/Au	5.04	0.69	63	2.19	[265]
FTO/c-TiO ₂ /Cs ₃ Sb ₂ I ₉ /Au	3.55	0.61	55.85	1.21	[266]
ITO/c-TiO ₂ /(N-EtPy)[SbBr ₆]/P3HT/Au	5.1	1.28	58	3.8	[267]

part of the review, two basic strategies to fabricate OPVs (solvent selection for active layer spin-coating and alternative green techniques) are discussed. Basic considerations and the main problems associated with each strategy are introduced first. Then, recent developments in the two main strategies for the improvement of the PCE of devices will be discussed.

Solvent Selection: Compared with toxic halogenated and aromatic solvents, green solvents are advantageous for industrial production that corresponds with sustainable development measures, as they decompose quickly; because the decomposition products are also environmentally friendly, the overall accumulation in the environment is reduced. However, active layer materials exhibit low solubility in green solvents at times, which can impact the efficiency of devices. HSP analysis can be introduced to screen for appropriate green solvents and

green-solvent processable materials, but for polymer donor materials, mismatched HSP is possible because of the indefinite molecular weight of polymers.^[283] Therefore, green solvents can be selected through empirical or trial-and-error methods by comparing their solution parameters with 1,2-dichlorobenzene, chlorobenzene (CB), and so on.

First, it is necessary to mention that the green solvents listed here are liquids of lower toxicity than halogenated solvents rather than well-defined solutions without toxicity. Based on their toxicity levels (from high to low), we can classify the processing solvents into four types, namely i) halogenated and aromatic, ii) non-halogenated and aromatic, iii) non-halogenated and non-aromatic, and iv) ketones, esters, alcohols, and water, as shown in **Figure 16**. Type (i) solvents are highly toxic and should be avoided in green processing. Therefore, in this

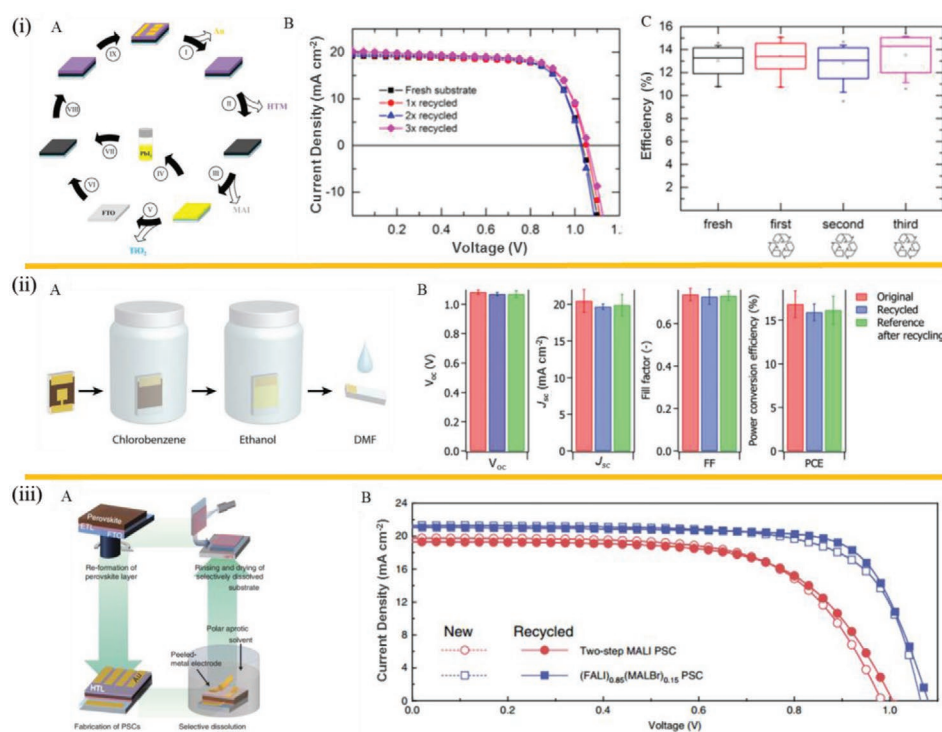


Figure 15. i) A: Recycling procedure for perovskite solar cells (PSCs). B: Current–voltage (J – V) characteristics of PSCs prepared on recycled fluorine-doped tin oxide (FTO)/glass substrates. C: Bar diagram of efficiency based on different numbers of rounds of recycling devices. Reproduced with permission.^[270] Copyright 2016, American Chemical Society. ii) A: Recycling process of FTO-coated glass substrates with mesoporous TiO₂. B: PSC performance of 30 samples before and after recycling. Reproduced with permission.^[271] Copyright 2016, Royal Society of Chemistry. iii) A: Detailed process of recycling PSCs via selective dissolution. B: Comparison of J – V curves between new and recycled MAPbI₃ and (FAPbI₃)_{0.85}(MAPbI₃)_{0.15}-based PSCs. Reproduced with permission.^[272] Copyright 2016, Nature Publishing Group.

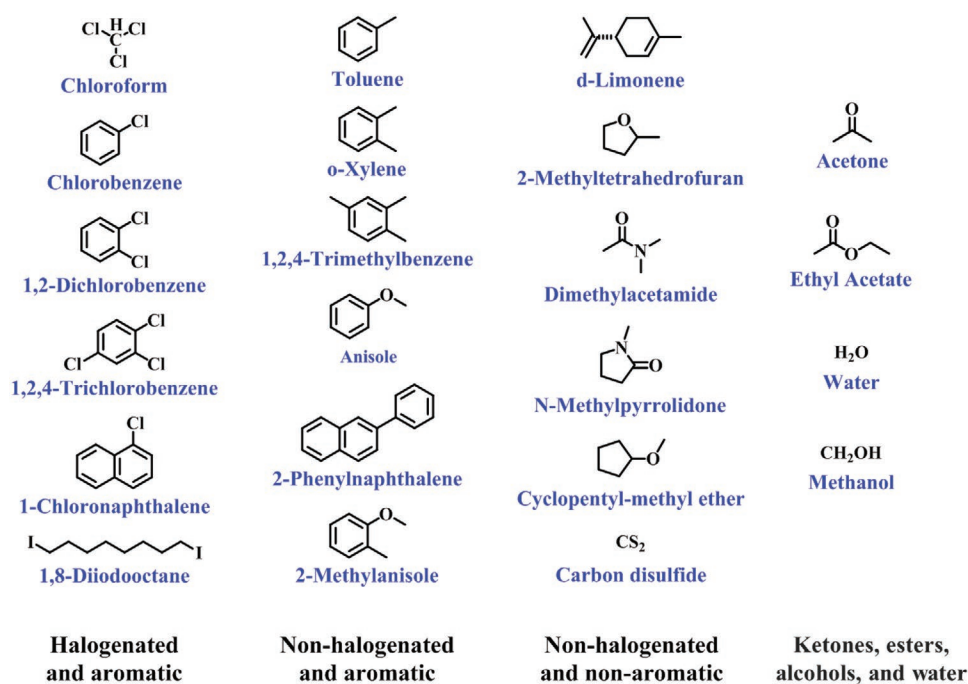


Figure 16. Four types of common solvents utilized in solution printing technique.

part of review, we will focus on recent research that discusses advances in the processing of OPVs using the other three types of solvents.

Non-Halogenated Aromatics: The most common non-halogenated aromatics used in OPV processing are TMB and *o*-XY. Kim et al. synthesized a new kind of donor polymer, P1, and blended it with PC₇₁BM to test in non-halogenated aromatic solvents (please note that the chemical structures of the polymers mentioned in this section are shown in **Figure 17**). After comparing the PCEs of the devices casted from CB (halogenated solvent) and *o*-XY (non-halogenated solvent), they found that the green solvent-processed OPVs demonstrated a PCE of 5.01% ($V_{oc} = 0.81$ V, $J_{sc} = 10.41$ mA cm⁻², and FF = 58.74%), which was comparable to that of the device processed with CB (PCE = 5.29%).^[284] Moreover, adding diphenyl ether (DPE) additive improved the solubility, as well as the efficiency, of the blended materials.

In fact, at times, it was difficult to remove high-boiling-point solvent additives and induce anomalous current–voltage (*J*–*V*) curves or low reproducibility. Therefore, a single green solvent was the best choice. Chen et al. designed two copolymer donors with random backbones, PBDB-2TC and PBDB-S-2TC. The random backbone conformation allowed the materials to dissolve in TMB. The devices fabricated with PBDB-2TC:ITIC or PBDB-S-2TC:ITIC exhibited high PCEs of 9.36% and 9.55%, respectively. These performances were comparable to that of the device obtained from casting with CB.^[285] Because of their excellent photoelectric properties, fluorine or sulfur atom-substituted BDT and 2TC were then combined with the same group to synthesize another two new copolymers, PBDB-F-2TC and PBDB-SF-2TC. For the devices fabricated with PBDB-F-2TC:IT-4F or PBDB-SF-2TC:IT-4F as the active layer casted from TMB, the PCEs obtained were 10.75% and 11.07%, respectively.^[286]

Non-Halogenated and Non-Aromatics: Chen et al. conducted HSP analysis on the solutes and solvents and predicted the optimal ratio for the mixture solvents. Efficiencies of 8.30% and 9.39% were obtained for the OPV devices fabricated with PTB7 and PTB7-Th, respectively, in which PC₇₁BM was used as the acceptor and 1,4-dioxane (DIOX) and terpinolene (TPO) were used as the non-halogenated and non-aromatic solvents, respectively. Although DIOX, as a single processing solvent, did not exhibit high efficiency in these two donor-based devices, a binary solvent that utilized both DIOX and TPO was found to be more effective. The PCEs of the two devices were both higher than their counterparts casted from CB.^[287] In another example, chloroform (CF) and carbon disulfide (CS₂) were used as the solvents in the small molecule OSCs. Peng et al. designed two innovative small molecules, namely BDTTNTTR and BDTSTNTTR, by using benzo[1,2-*b*:4,5-*b'*] dithiophene (BDT) as the central core. The PCEs of the devices fabricated with the small molecules as donors and PC₇₁BM as the acceptor processed with CF were 8.06% and 9.71%, respectively, which increased to 10.02% and 11.53%, respectively, when the solvent was changed to CS₂.^[288] In addition to applying green solvents to dissolve small-molecule/polymer active materials, significantly, molecular design strategies are also the key method for simultaneously improving efficiency and green processability. Hou's group successfully applied alkyl side chain modification and ternary copolymerization strategies to improve the

solubility of active materials into non-halogenated and non-aromatic solvents, achieving high performance of polymer solar cells.^[289,290] For side chain modification strategy, polymer donor material (PBDB-BzT) was synthesized by modifying flexible alkyls side chain of poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene)-*co*-(1,3-di(5-thiophene-2-yl)-5,7-bis(2-ethylhexyl)-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione))] (PBDB-T), improving the solubility and enhancing aggregation effect in tetrahydrofuran (THF). An impressive PCE of 12.10% was achieved with PBDB-BzT:3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6/7-methyl)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-*d*:2',3'-*d'*]-*s*-indaceno[1,2-*b*:5,6-*b'*] dithiophene (IT-M) blends under THF solvent.^[289] For ternary copolymerization strategy, ester group-substituted thiophene (EST) unit into the benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT)–benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (BDD) alternating polymer PBDB-TF donor was proposed by copolymerization strategy. Significantly, the proposed copolymer showed high solubility in THF/NMP non-halogenated and non-aromatic solvents. Excitingly, copolymer PBDB-TF:IT-4F blends with THF/NMP solvents showed 14.2% in 0.0375 cm² and 13.7% in 1.07 cm².^[290] Therefore, in-depth study of the correlation between molecular structure/functional groups in active materials and green solvents followed by designing/modifying molecular functional groups are effective strategies to improve the solubility in green solvents and efficiency for green processing.

Ketones, Esters, Alcohols, and Water: Ketones, esters, alcohols, and water are the least toxic of the four types of solvents reviewed; therefore, they are highly desirable as green solvents to dissolve donor/acceptor materials. However, the ion group substituted materials exhibit very low photoelectric responses because the ionic and related groups can trap or quench the charges.^[291] Therefore, solution deposition with these green polar solvents is quite challenging. Nevertheless, Kim et al. developed an aqueous processing method for the eco-friendly fabrication of polymer photovoltaics, which shows great potential for application on an industrial scale. The oligoethylene glycol side chain-based donor/acceptor, polymer PPDT2FBT-A and fullerene PC₆₁BO₁₂, can be dissolved in a 1:1 (molar ratio) water-ethanol mixed solvent. The maximum PCE of the fabricated device is 2.05%.^[292] In another example, Di-Nicola et al. fabricated devices with the water-soluble donor materials, poly[3-[(6-sodium sulfonate)hexyl]thiophene] (PT6S) and poly[3-[(6-trimethylammoniumbromide)hexyl]thiophene] (PT6N), which can both act as a charge collection layer. Processed by H₂O/H₂SO₄ (pH = 1), the device (with a structure of ITO/PT6S/PT6H-PCBM 1:1 w/w/PT6N/Al) yields a higher PCE of 4.78%.^[293] However, the performance of devices processed with such polar and low/non-toxic solvents is still behind the non-halogenated aromatic, and non-halogenated and non-aromatic solvent processing devices, mainly owing to the limited selectable active materials to dissolve in ketones, esters, alcohols, and water. Molecular design or modifying is a promising strategy with the purpose to improve the polarity of high-performance active materials, and enhance the solubility in ketones, esters, alcohols, and water.

Table 4 summarizes the performances of reported OPVs processed with different types of green solvents by solvent engineering strategy or material design strategy. Despite some devices with a low efficiency, several devices yielded a decent

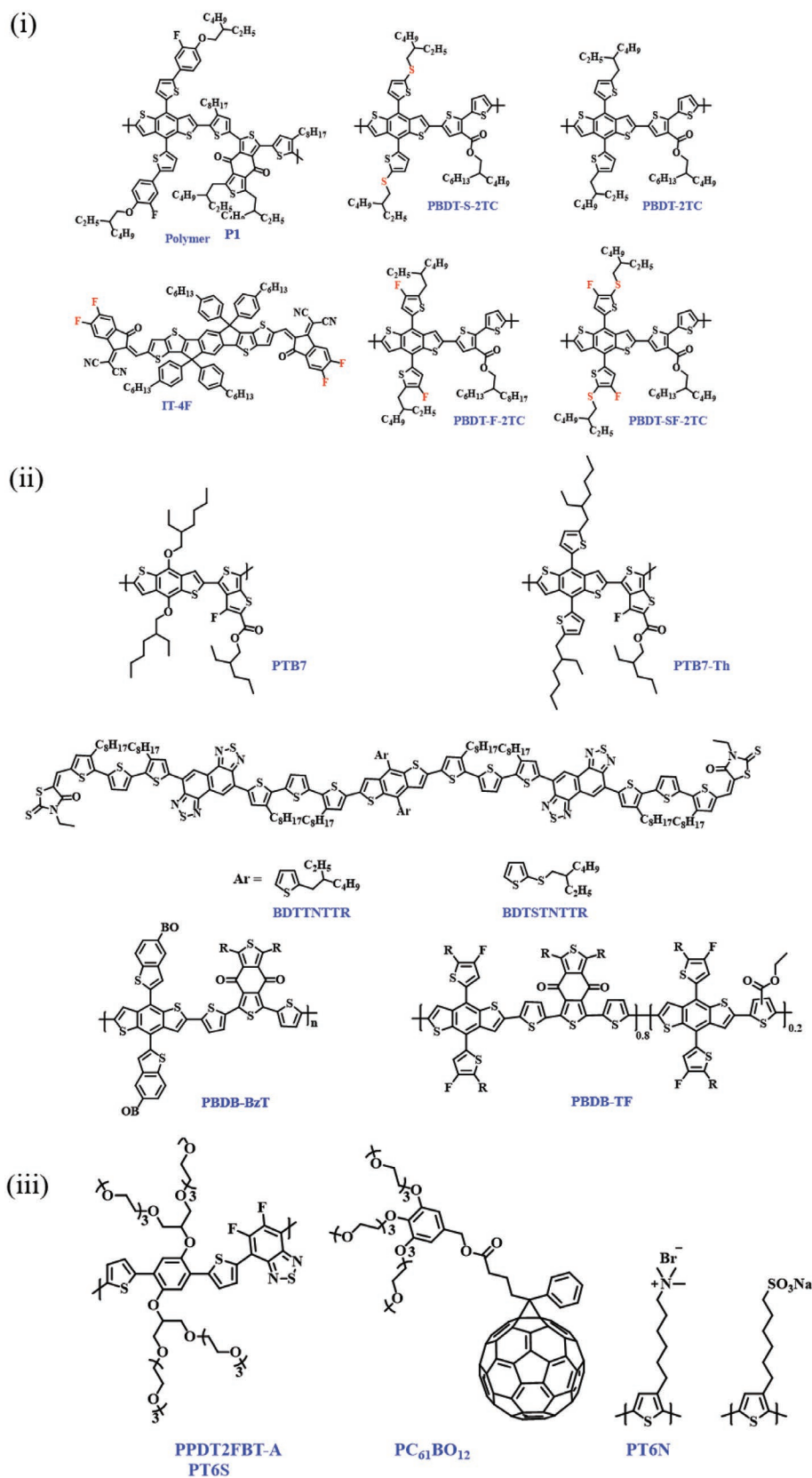


Figure 17. Chemical structure of light-harvesting materials soluble in i) non-halogenated and aromatic solvents; ii) non-halogenated and non-aromatic solvents; iii) ketones, esters, alcohols, and water solvents.

Table 4. Summary of recently reported performances of organic photovoltaics (OPVs) by using green solvents.

	Light-harvesting layer	Solvent	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]	Ref.
Non-halogenated aromatic	d1:PC ₇₁ BM	<i>o</i> -XY/DPE	0.81	10.41	58.74	5.01	[284]
	PV2000:PC ₇₁ BM	<i>o</i> -XY	0.772	20.1	65	10.1	[294]
	poly(3HTBT-TPA):PC ₇₁ BM	<i>o</i> -XY	0.86	6.61	42	2.39	[295]
	<i>p</i> -DTS(FBTTh ₂) ₂ :NIDCSN	<i>o</i> -XY	1.04	5.41	52	2.92	[296]
	DPPEZnP-O:PC ₆₁ BM	<i>o</i> -XY + 1% MN + ANN	0.75	15.73	50	5.75	[297]
	PTB7:PC ₇₁ BM	<i>m</i> -XY	0.704	16.56	56.98	7.05	[298]
	PBDTTT-CT:PC ₇₁ BM	<i>m</i> -XY + DIO	0.771	14.39	64.45	7.1	[299]
	poly(3HTBT-TPA):PC ₇₁ BM	TMB	0.85	6.31	40	2.15	[295]
	PBDT-2TC:ITIC	TMB	0.903	16.87	61.46	9.36	[285]
	PBDT-S-2TC:ITIC	TMB	0.919	17.32	60.05	9.55	[285]
	PBDT-F-2TC:IT-4F	TMB	0.917	18.9	62.51	10.75	[286]
	PBDT-SF-2TC:IT-4F	TMB	0.936	20.73	57.45	11.07	[286]
	N(Ph-2T-DCN-Et) ₃ :PC ₇₁ BM	Benzaldehyde	0.96	8.27	46.75	3.71	[283]
	N(Ph-2T-DCN-Et) ₃ :PC ₇₁ BM	Benzaldehyde/ mesitylene	0.96	8.37	46.68	3.75	[283]
	PTB7-Th:PDl ₂ -R	TLN	0.96	12.4	47	5.4	[300]
	<i>p</i> -DTS(FBTTh ₂) ₂ :NIDCSN	TLN	1.08	6.06	50	3.30	[296]
	DPPEZnP-O:PC ₆₁ BM	TLN + 1% MN + ANN	0.77	14.7	48.3	5.46	[297]
	P3HT:PC ₆₁ BM	Anisole:THN	0.57	9.09	65	3.37	[301]
	PBDTTT-C:PDlate	Anisole	0.71	1.91	33.1	0.45	[302]
	PBDTTT-C:oo-2PDlate	Anisole	0.676	8.76	37.9	2.24	[302]
	PTB7:P(NDI2OD-T2)	2-Methyl anisole	0.76	15.40	58.03	6.79	[303]
	P3HT:P(NDI2OD-T2)	2-Methyl anisole	0.68	12.9	63.84	5.6	[304]
Non-halogenated and non-aromatic	PTB7:PC ₇₁ BM	DIOX/TPO	0.76	15.34	71.19	8.30	[287]
	PTB7-Th:PC ₇₁ BM	DIOX/TPO	0.80	17.2	68.26	9.39	[287]
	BDTTNTTR:PC ₇₁ BM	CS ₂	0.89	15.70	71.7	10.02	[288]
	BDTSTNTTR:PC ₇₁ BM	CS ₂	0.93	16.21	76.5	11.53	[288]
	<i>p</i> -DTS(FBTTh ₂) ₂ :NIDCSN	THF	1.07	5.23	54	3.02	[296]
	BDT3TR-SF:NBDTP-Fout	THF	0.798	21.87	64.37	11.2	[305]
	HFAQx-T:N2200	THF	0.92	12.47	65	7.45	[306]
	HFQx-T:N2200	THF	0.90	11.69	59	6.2	[306]
	PBDB-BzT:IT-M	THF	0.96	17.97	70	12.10	[289]
	PBDB-TF:IT-4F	THF/NMP	0.887	21.1	76	14.2	[290]
	PBTA-TF:IT-M	THF/IPA	0.96	18.37	67	12.0	[307]
	PTB7-Th:tPDI-Hex	Me-THF	0.94	11.6	43.7	4.8	[308]
	PTB-EDOTS:ITIC-Th:J71	Me-THF	0.90	18.02	75.6	12.26	[309]
	PTzBI-Si:PBTA-Si:N2200	Me-THF	0.85	14.89	75.65	9.56	[310]
	PBTA-PEG-2%:N2200	Me-THF	0.83	16.89	66.13	9.27	[311]
	FTAZ	(R)-(+)-limonene/ Me-THF	0.958	18.3	70	12.5	[312]
	PBDTTTTEG:PC ₇₁ BM	NMP	0.66	13.53	58.55	5.23	[313]
	PBDTTTTEG:PC ₇₁ BM	NEP	0.66	13.74	56.18	5.06	[313]
	PTB7:PC ₇₁ BM	TPO	0.77	13.5	61.6	6.42	[314]
Ketones, esters, alcohols, and water	PPDT2FBT-A:PC ₆₁ BO ₁₂	Water/ethanol	0.76	5.08	53	2.05	[292]
	P3HT:PC ₆₁ BM	SDS-water/chloroform	0.38	7.1	44	1.2	[315]
	PCDTBT:PC ₇₁ BM	CS ₂ /acetone	0.91	10.72	68.20	6.62	[316]
	PT6H-PC ₆₁ BM	H ₂ O/H ₂ SO ₄ (pH = 1)	0.65	13.11	56	4.78	[293]

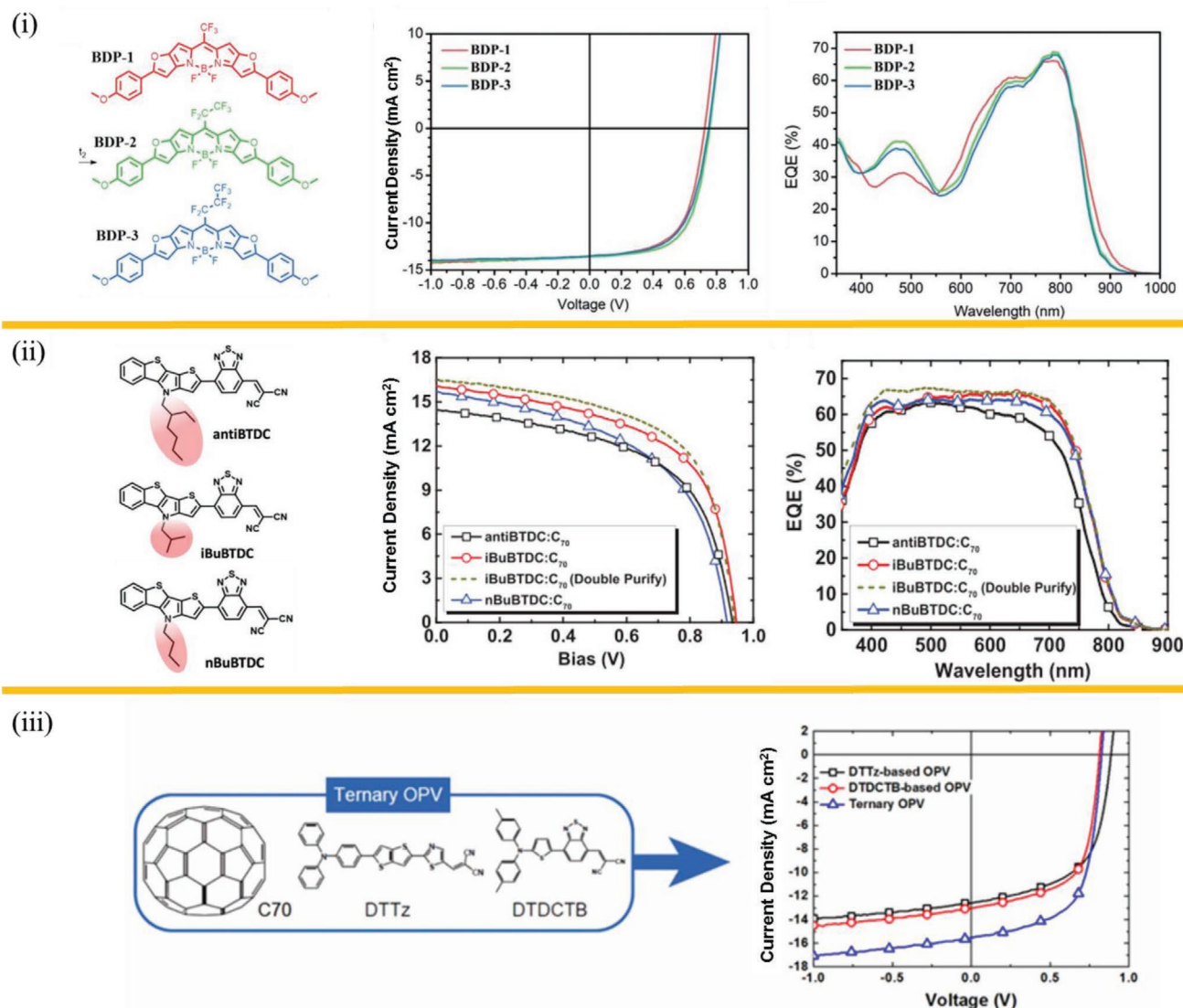


Figure 18. i) Molecular structural formulae of boron dipyrromethenes and corresponding solar cell performances. Reproduced with permission.^[318] Copyright 2018, Royal Society of Chemistry. ii) Molecular structural formulae of antiBTDC, iBuBTDC, and nBuBTDC and corresponding solar cell performances. Reproduced with permission.^[319] Copyright 2018, Wiley-VCH. iii) Ternary organic photovoltaic (OPV) with two donors, DTTz and DTDCTB; one acceptor, C₇₀; and corresponding solar cell performances. Reproduced with permission.^[320] Copyright 2016, American Chemical Society.

efficiency (near to or greater than 10%), indicating good potential for their use as green solvents in the processing of OPVs.

Alternative Green Techniques: Vacuum deposition is an alternative green technique that avoids the use of toxic solvents and offers a unique advantage of accurate thickness controllability in multi-layer device fabrication.^[318] Li et al. synthesized boron dipyrromethene with mesoperfluorinated alkyl substituents and used near-infrared-absorbing donors in vacuum-deposition processing. The fabricated solar cells achieved an efficiency greater than 6.0% with the highest EQE of 70%, as shown in Figure 18-i.^[318] Forrest et al. conducted vacuum deposition to fabricate OPVs based on donor–acceptor–acceptor type small molecular semiconductors. By varying the side chains, isobutyl substituted iBuBTDC was found to pack densely, and the resulting device achieved the highest PCE of 9.3% (Figure 18-ii).^[319]

Moreover, Kim et al. fabricated ternary OPV devices by vacuum deposition of two donors and a C₇₀ acceptor (Figure 18-iii). In the active layer, 2-((2-(5-(4-(diphenylamino)phenyl)thieno[3,2-b]thiophen-2-yl)thiazol-5-yl)methylene)malononitrile (DTTz) and 2-((7-(5-(dip-tolylamino)thiophen-2-yl)benzo[c]-[1,2,5]thiadiazol-4-yl)methylene)malononitrile (DTDCTB) were used for visible and near-infrared absorption, respectively.^[320] The obtained PCE of 8.02% demonstrated the potential of vacuum deposition in ternary OPV device fabrication.

3.2. Green Processing of OFETs

In the fabrication of OFETs, spin-coating is a low-cost, simple, and effective way to form a uniform semiconductor thin film.

Although halohydrocarbon and arene are commonly used and considered good solvents for most conjugated organic semiconductors, the harm caused by them to the environment and human beings is non-negotiable. Halohydrocarbon and arene are both carcinogens, which pose a great threat to health. In addition, halohydrocarbon is degradation-resistant and will destroy the ozonosphere and cause the greenhouse effect upon accumulation. Considering these circumstances, safe solvents including alcohols, esters, and water are favored. However, the solubility of organic semiconductors in these safe solvents is unsatisfactory. Therefore, scientists are trying to introduce an appropriate functional group into semiconductors to obtain good solubility in green solvents.

One possible method is the introduction of ionic side substituents to hydrophobic backbones. However, these ionic groups are only stable in certain pH conditions, which impedes the aggregation of the polymers.^[321] Another drawback of these ionic groups is that they may mingle to active layers of the OFETs, which may decrease their stability.^[322] Therefore, another approach was adopted that involves attaching some high polar, neutral side groups to π -conjugated backbones to increase the water solubility of the polymers.^[323] The introduction of hydrophilic 3-(2-(2-(2-methoxyethoxy)ethoxy)methyl side chains to polythiophene produces the polymer, P3TEGT, which joins water as the green solvent in the fabrication of OFET devices and exhibits a hole mobility of $3.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under ambient conditions.^[324] Further decrements in the side chain length may improve this mobility.

Another group introduced a similar type of side chains to a non-ionic polymer, poly[(2,5-bis(1,3-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)propan-2-yloxy)phenylene)-alt-(5,6-difluoro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)] (PPDT2FBT-A), which exhibits good solubility in ethanol. The fabricated OFET, with simple ethanol as the solvent, exhibits a high hole mobility of $1.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ because of the high edge-on oriented crystalline nature of PPDT2FBT-A films spin-coated from ethanol solutions.^[325] However, the mobility of green solvent processed OFETs is still lower than that of traditional devices processed from toxic solvents such as CB, TLN, and CF. Additionally, unlike OPVs and PSCs, the development of green processing and semiconducting materials that are compatible with green solvents are very limited, and more efforts should be directed to this area to fulfill the realization of truly green electronic devices.

3.3. Green Processing of LEDs

3.3.1. Inorganic LEDs

The toxic solvents and heavy metals used in the preparation of light-emitting devices have resulted in serious harm to both humans and the environment. There have been numerous reports exploring potential green solvents and low-toxicity materials for use in the preparation process of LEDs. Although WLEDs have offered a promising technique in regard to sustainability because of their advantages in working lifetime and electricity consumption, the cost of conventional phosphors as color converters has remained high and some rare-earth raw materials were required. To address this problem, Zeng et al.

synthesized intercrossed carbon nanorings (IC-CNRs) as the phosphors; these IC-CNRs were not only low-cost because of their simple synthesis, but they were also environmentally friendly.^[149] The obtained color coordinates (0.28, 0.27) for the device based on IC-CNRs were observed to be comparable to those of the WLEDs (0.33, 0.33). Recently, yellow carbon quantum dots (Y-CDs) were prepared by Zhong et al., and water and *o*-phenylenediamine were used as the solvent and carbon source, respectively.^[326] A yellowish luminescence with long wavelength was easily achieved with the resulting Y-CDs thin films. Besides carbon-based materials used as color converters in WLEDs, Chao et al. fabricated WLEDs based on a blend of Au nanoclusters and blue-emitted organic materials that obtained color coordinates (0.27, 0.33).^[327] The Au nanoclusters were modified with triethylphosphine capping groups that were non-toxic and eco-friendly. The recently discovered $\text{A}_2\text{MF}_6\text{:Mn}^{4+}$ material, which exhibits superior photoluminescent properties, is considered a promising alternative to commercial phosphors. Wu et al. reported that $\text{K}_2\text{SiF}_6\text{:Mn}^{4+}$ (as a red emitter) can be synthesized with a green process in which $\text{H}_3\text{PO}_4/\text{KHF}_2$ liquid is used to replace the hydrogen fluoride (HF) solvent, thereby avoiding toxicity and volatility.^[328] Xu et al. recently reported the utilization of tetramethyl-substituted aluminium phthalocyanine (AlMePc) as the modification layer of ITO electrodes in OLEDs. AlMePc allows green solvent processing in alcohol and is helpful in promoting balanced charge carrier injection and transport, thereby demonstrating higher device performance and green processing fabrication of OLEDs.^[329]

3.3.2. Quantum Dots and Perovskite LEDs

As for next-generation light-emitting techniques such as quantum dots LEDs (QLEDs) and perovskite LEDs (PeLEDs), there remain solution processes during fabrication that contain toxic materials. Ray et al. replaced toxic phosphine with olive oil as the capping agent to synthesize CdSe QDs, and the material showed a sharp and well-defined emission peak of 568 nm at room temperature.^[330] Later, Yu et al. fabricated low-toxicity $\text{AgIn}_5\text{S}_8/\text{ZnS}$ -based QLEDs that exhibited a significantly enhanced efficiency after surface treatment with 1,2-ethanedithiol.^[331] Similar to PSCs, the B-site in the ABX_3 structure was typically heavy metal Pb^{2+} , and some researchers have made an effort to replace it with other low-toxicity metals, such as Sn,^[332,333] Sb,^[334,335] and Bi.^[336–339] Additionally, the antisolvents used in the synthesis of perovskite thin film or nanocrystals are typically TLN and CB. Because of the toxicity of TLN, Yang et al. employed tetraethyl orthosilicate as the antisolvent to achieve all-inorganic perovskite nanocrystals which presented tunable large-span emission wavelengths in the range of 626–437 nm.^[340] Recently, Yu et al. applied isopropyl alcohol (IPA) as the antisolvent to fabricate PeLEDs, which exhibited good performance; the maximum luminance, current efficiency, and turn-on voltage were $7\,960 \text{ cd m}^{-2}$, 2.2 cd A^{-1} , and 2 V, respectively.^[341] The results indicated that high efficiency devices could be fabricated with a green solvent. In future development, the trade-off between green processing and the performance of devices needs consideration, and a push for eco-friendly, light-emitting devices over commercial products is necessary.

3.4. Green Processing of Other Devices

Other devices (e.g., batteries, sensors, generators, memristors, and photodetectors) are also suitable for green processing with low-toxicity materials and low-cost fabrication to achieve green electronics.^[342–345] Aqueous lithium-ion batteries that use water-based electrolytes are a promising alternative to address the issues of safety and environmental problems caused by highly toxic and flammable organic electrolytes.^[346] Currently, the highest operating voltage of aqueous lithium-ion batteries exceeds 4 V by using a graphite-based cathode with bromine and chlorine that is protected by the water-based electrolytes through confining reactive electrode materials in the solid salt particles around the electrode.^[347] Moreover, water-based concepts can be applied to a triboelectric nanogenerator (TENG), which is a promising energy harvesting technology that efficiently converts ambient mechanical energies into electricity. Hao et al. applied physical-crosslinking PVA hydrogel as a substrate material to fabricate fully flexible and environmentally friendly TENG. This hydrogel-TENG is not only low in cost, but it can also utilize the energy harvested from human motions (i.e., bending, twisting, and stretching), thereby achieving a self-powered sensor.^[348] Nanomaterial green printing, which greatly reduces energy consumption and environmental pollution from the sources, is a promising green process to fabricate electronics. However, the challenge in this technique is that liquids must work on very small scales, which is virtually impossible, owing to the fact that the conventional nozzle has a minimum of 10 μm droplets. Song et al. developed a novel gas–liquid–solid three-phase contact line (TCL) that can be manipulated to assemble and deposit the nanoparticles covered by the liquid droplet following the TCL pattern, obtaining a nanoscale conductive curve array.^[349,350] In this manner, they introduced Ag nanoparticles on a PDMS substrate. The fabricated flexible sensors have been applied to human facial skin and can deliver real-time data for multi-analysis of human skin micromotions.^[351]

4. Conclusion and Outlook

E-waste resulting from the rapid development of the electronics industry is a real and urgent issue that needs to be addressed. Green electronics is an effective way to manage e-waste through the use of biodegradable materials and green fabrication processing. In addition to microminiaturization, integration, and multi-functionalization, greenization is one of the most vital movements concerning the future e-market. Fortunately, research communities are aware of the importance of green electronics and have taken action to achieve this goal. This review summarizes the most current biodegradable materials and green processes for green electronics, including solar cells, OFETs, LEDs, and other electronic devices. The reports herein provided comprehensive knowledge regarding the potential for the fabrication of green electronics.

With regard to the biodegradable materials used in green electronics, both natural and synthesized biodegradable materials can be used as substrates, electrodes, and active materials. At present, the most widely studied biodegradable materials are cellulose, chitosan, and SF. For the green process, low-toxicity

materials or solvents that incur low-costs and are capable of large-scale implementation are acceptable solutions for the fabrication of green electronic devices. However, biodegradable materials and green process-based electronics are still in their infancy. Moreover, the performance of green electronic devices is not yet up to par with conventional devices, owing to the limitations of the selective biodegradable materials and undeveloped green processing. The database of biodegradable materials needs to be expanded by further studying the physicochemical characteristics of various substances and the corresponding performances they induce in devices. Indeed, synthesized organic materials are promising biodegradable candidates for high-performance electronics, but the synthetic processes are usually associated with non-green methods involving toxic solvents. Therefore, the design of green electronics with biodegradable materials should take the green process into consideration. Further, recycling different functional layers in devices is also a key solution to reduce e-waste and the cost of devices.

Efficacy, stability, and environmental friendliness are crucial factors in determining the potential of commercialization and widespread use of green electronics in the future. Based on these concepts, guidelines for the green electronic design are as follows:

Deeply study and modify existing biodegradable natural/synthesized materials to enhance their biodegradation in mild conditions, so they can be used as biocompatible and biodegradable substrates.

Change the molecular bonds of conductive organic materials through chemical modification, rendering them sensitive to weak acids while retaining their ability of fast charge-transfer, which can be used as active layers with high performance.

Develop non-noble metals (e.g., Fe and Mg) with environmentally friendly and non-toxic properties that are harmless to humans, can be used as electrodes, and are easily degraded in a mild acid/base or water solution.

Combine the HSP model with drying kinetics to predict the solubility of solutes in low/non-toxic green solvents.

Modify the chemical structure of existing high-performance materials through the introduction of polar functional groups, thereby increasing the solubility in polar green solvents.

Explore and develop non-toxic, solvent-free, annealing-free, and low-cost alternative manufacturing processes to fabricate green electronics.

Overall, we need to face up to the environmental issues caused by the conveniences of modern electronics. The significant progress achieved in green electronics is very encouraging, especially the development of high-performance green electronics fabricated with biodegradable materials through green processing. “Treatment after pollution” is inadvisable for sustainable development. Therefore, more efforts are necessary for the integrative exploration combining biodegradable materials and green processing for the fabrication of future green electronics.

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] Consumer Electronics Market by Product (Smartphone, Television, DVD players, Refrigerators, Washing machines, Digital cameras, and Hard disk drives) and by Region (North America, Europe, Asia Pacific, Latin America, and the Middle East & Africa)—Global Industry Perspective, Comprehensive Analysis and Forecast, 2017–2024, Zion Market Research [Online], <https://www.zionmarketresearch.com/report/consumer-electronics-market> (accessed: June 2018).
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