Published in final edited form as:
Polym Int. 2010 May 1; 59(5): 563–567. doi:10.1002/pi.2827.

Biomaterials-Based Organic Electronic Devices

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Abstract

Organic electronic devices have demonstrated tremendous versatility in a wide range of applications including consumer electronics, photovoltaics, and biotechnology. The traditional interface of organic electronics with biology, biotechnology, and medicine occurs in the general field of sensing biological phenomena. For example, the fabrication of hybrid electronic structures using both organic semiconductors and bioactive molecules has led to enhancements in sensitivity and specificity within biosensing platforms, which in turn has a potentially wide range of clinical applications. However, the interface of biomolecules and organic semiconductors has also recently explored the potential use of natural and synthetic biomaterials as structural components of electronic devices. The fabrication of electronically active systems using biomaterials-based components has the potential to realize a large set of unique devices including environmentally biodegradable systems and bioresorbable temporary medical devices. This article reviews recent advances in the implementation of biomaterials as structural components in organic electronic devices with a focus on potential applications in biotechnology and medicine.

Introduction

Organic electronic devices have demonstrated tremendous versatility in a wide range of applications including consumer electronics, photovoltaics, and biotechnology.[1] Recent advancements into the latter have led to the development of systems that are able to efficiently interface biological events with electronic devices.[2] This progress has led to the continued maturation of biological sensing platforms with potential applications in rapid screening of biological samples and point-of-care diagnostics. Biosensor platforms typically function as transducers that map chemical events, such as analyte binding or DNA hybridization for example, to electrical signals. Efforts in these areas have createda unique opportunity to interface biological systems and organic electronic devices. However, concurrent advancements in biomaterials processing and organic electronic device development have allowed for the integration of biomolecules as a materials set with which to fabricate devices. Of particular interest is the potential to fabricate biomaterials into the structural components of organic electronic devices. In principle, it is possible to fabricate biomaterials into each of the major materials sets that are employed in construction of an organic transistor including the bulk substrate, dielectric interface, and even the active semiconducting layers and electrodes. This review of recent work highlights recent advancements in processing natural and synthetic biological materials as structural components of organic electronic devices. Particular interest will focus on the adaptation of biodegradable materials for potential use in implantable biomedical devices.

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Biomaterials as Structural Components in Organic Electronic Devices

Advances in substrate development have been directed at expanding the overall functionality of the super-positioned organic electronic devices. For example, efforts to fabricate flexible electronic circuits were focused on developing processes that are compatible with flexible plastic substrate materials such as poly(ethylene terephthalate) (PETE).[3] However, the realization of these systems requires processes that are compatible with the underlying substrate including, in the case of PETE, such limitations as using mild, aqueous solvents and low-temperature post-processing. The additional capability of fabricating organic electronic devices on flexible substrates including displays and photovoltaics has immediate and obvious implications in consumer electronics including expanded portability and conformability. Other capabilities have been explored to realize electronic circuits that are not only flexible, but also foldable. Substrate materials such as aluminum foil[4] and paper[5] have been studied to accommodate these expanded functionalities. In one embodiment of this idea, paper films were utilized as a combination substrate and gate dielectric for use with pentacene-based active layers.[5] This idea was expanded upon to create complete circuits using foldable paper-based substrates. This demonstration was motivated by two primary factors: 1) paper substrates are mechanically flexible and capable of small bending radii;2) paper is ubiquitous in modern society. As such, utilizing paper-based substrates are a potentially very important strategy for widespread deployment of simple electronic devices. A wide range of functionality is demonstrated including the ability to fabricate circuits on rolls of paper that can be easily crafted into the final form by virtue of simple folding and cutting techniques (Figure 1a). One can even imagine interfacing circuit design and layout with origami to develop circuits with unique topologies(Figure 1c). The relative fragility of paper-based circuits could also be potentially utilized in security applications. One specific example mentioned is the fabrication of a envelope integrated with a circuit that, if compromised via destruction of the envelop, will cease to function. Paper-based devices also present distinct advantages in terms of disposability. Paper-based circuits could be both combustible and environmentally biodegradable. The concept of biodegradable substrates for electronic circuits has also been explored in the context of biomaterials. The motivation of this nascent research topic is to explore the intersection of biomaterials and electronic devices for potential applications in restorable electronically active medical implants, for example. Recent developments have explored the potential use of mechanically robust, water insoluble, natural proteins as substrates for silicon electronics. The work of Kim et al. describes the use of silk fibroin as a substrate for traditional silicon-based transistors. The performance of these devices is only mildly impacted upon mechanical deformation of the substrate(Figure 2). The biocompatibility profiles observed in this study suggest that this and similar devices may be able to be implanted with minimal deleterious tissue interactions.

Biomaterials as Active Components

Insulators and Dielectric Materials

Biomaterials present a wide range of material properties that may be suitable for use in functional materials within organic electronic systems. The vast majority of natural and synthetic polymeric biomaterials are electrically insulating and therefore possess suitable material properties for gate dielectrics and semiconductor-interface engineering. For example, poly(vinyl alcohol) (PVA) is a highly polar water-soluble polymer with a large dielectric constant.[6] PVA can also be used in combination with photosensitizers such as ammonium dichromate to enable a simple photolithographic dielectric material platform. These collective properties suggest that PVA is amenable for use as an insulating material in organic electronics. PVA has been extensively characterized as a gate dielectric material for several semiconductor systems including pentacene and *para*-hexaphenyl.[6] Potential pitfalls with PVA include significant hysteresis and potentially large gate leakage currents. PVA has also been explored as a biomaterial for many applications including drug delivery[7] and hydrogel networks[8] because of its ability to be bio-excreted and biodegraded.[9, 10] These combined characteristics suggest that PVA may also be a suitable insulating material for the next generation of bioresorbable organic electronic devices.. The insulating properties of most natural biopolymers suggests other materials may also be used as dielectric interfaces. For example, recent work has demonstrated that DNA molecules can be processed into gate dielectrics.[11] Aqueous solutions of high molecular weight (Mw = 8,000,000 Da) DNA and hexadecyltrimethylammmonium chloride (CTMA) were processed into films of approximately 500 nm in thickness on to ITO-coated glass substrates. The DNA-CTMA films could also be crosslinked using poly(phenylisocyanate-co-formaldehyde)(PPIF)to create more mechanically robust films that are more solvent-resistant to downstream processes. The dielectric constant of crosslinked DNA-CTMA films was measured to be 5.4 which is sufficient for use as a gate insulator. Top-contact transistor structures were fabricated with DNA-CTMA gate dielectrics by using either C_{60} or alpha-T6 as the active layer and gold source-drain electrodes. OTFTs fabricated using crosslinked DNA-CTMA gate dielectrics exhibited reduced hysteresis with only modest changes in electron or hole mobilities. The broader implications of these works suggest that, generally speaking, biomolecules exhibit the appropriate set of properties to potentially function as critical circuit elements within organic electronic systems.

Semiconductors

While the vast majority of natural biomaterials are insulating, there are a few notable examples of semiconducting biomolecules with potentially intriguing electronic properties. Perhaps the most widely studied naturally occurring class of semiconducting biomaterials are melanins, an ubiquitous pigment found within mammals.[12] In fact, some of the initial discoveries of semiconducting organic solids were made using melanin as a model material.[13] Since that time, melanin has been explored as both a biochemical entity as well as an engineering material. Recent work has been focused on studying electronic conduction mechanisms of melanin,[14] processing capabilities,[15] and even potential use as a material for regenerative medicine applications.[16] To date, most melanins including eumelanin are classified as ohmic materials[17] due to the high degree of overlapping electronic structures,[18] which is likely to be derived from the highly disordered chemical structure. The overall disorder of the structure reduces the potential for use of melanin as active materials in devices such as organic transistors, for example. However, there are other classes of molecules that may potentially serve as active layers in future biomaterials-based organic electronic devices. Carotenoids, a class of naturally occurring small molecule pigments, have been studied as potential use in OTFTs.[19] Carotenoids are small molecule polyenes that serve as precursors for many biomoleules including Vitamin A. Bixin and beta-carotene, two specific types of carotenoids, were processed from solution to form OTFTs which exhibited hole mobilities on the order of 10^{-6} and 10^{-7} cm^2-V^{-1}-sec^{-1}, respectively. While the electrical performance of these specific materials may not be yet suitable for particular device applications, this work demonstrates the wide range of electronic properties that biomaterials can possess. These intriguing results generally suggest that the study of electron conduction mechanisms and structure-function-property relationships in semiconducting biomaterials may not only yield insight into their biological role, but may also prove to be technologically useful as materials in next-generation organic electronic devices.

Device Integration Using Biomaterials

Packaging Materials

Packaging of electronic devices in general, and organic electronic devices in particular, is an important and complimentary thrust in organic electronics. Many conjugated organic compounds used in the active layer of OTFTs are susceptible to oxidation and loss of function in ambient and aqueous environments. Packaging strategies typically involve the encapsulation of the entire device in biocompatible polymers such as parylene-c.[20] More recent work has evaluated the use of poly(vinyl acetate) (PVAc) as an encapsulation material.[21] Pentacene transistors encapsulated with PVAc were found to maintain performance after exposure to ambient conditions and cyclical mechanical bending. This study suggests that biodegradable polymeric packaging materials may also be used to maintain the functionality of organic electronic devices that are exposed to harsh conditions such as aqueous solutions, high salinity environments, and elevated temperatures. One particular concern will be to ensure that these encapsulation materials will be able to repel liquid water and water vapor for time scales on the order of months. Biodegradable polymers with high crystallinity, high hydrophobicity, and facile processing will likely be utilized to meet this demand. One example may be the use of poly(L-lactide) which satisfies all the aforementioned criterion and can be processed through melt casting or the use of common organic solvents.

Biodegradable Electronic Devices

The convergence of biodegradable materials and organic semiconductors yields abundant opportunities to produce electronic systems with unique overall material profiles. One particularly intriguing concept is the notion of fabricating fully bioresorbable electronic devices for potential use in temporary electronically active medical devices. Towards this end, recent efforts have focused on the fabrication of OTFTs in a fully biodegradable platform as a proof of concept. Initial iterations of this concept utilize synthetic biodegradable polymers that are both ubiquitous in medical applications and exhibit appropriate electronic properties.[22] Poly(DL-lactide-co-glycolide) (PLGA) was melt processed to form the device substrate, which comprised over 99% of the device by mass. Solution-processed PVA was selected as the gate dielectric because of its demonstrated advantages in electronic and biomedical applications. The active layer consisted of hydrophobic small molecule semiconductor that has previously demonstrated stable operation in aqueous environments.[23] While the biodegradation of the small molecule active layer has not been studied explicitly, it is hypothesized that the chemical breakdown of polyaromatic small molecules would commence via oxidative biodegradation processes within perioxisome organelles; [24] processes that are similarly responsible for the free radical degradation of naturally occurring polyaromatic melanins. The top-contact OTFT device structure was completed by the use of silver and gold as the gate and source-drain contacts, respectively. These devices exhibited suitable device operation with hole mobilities up to0.2 cm^2-V^{-1}-sec^{-1} and I_{on}-I_{off} ratios on the order of 10^3. OTFTs fabricated using UV-photocrosslinked PVA gate dielectrics maintained function after direct exposure to liquid water. *In vitro* biodegradation of these devices was demonstrated by incubation in citrate buffer. Device functionality was lost almost immediately while device disintegration occurred after approximately 50 days. This demonstration is only the first step toward the realization of fully biodegradable organic electronic systems. Ideal devices for these applications will be able to operate using low-voltages and be integrated with suitable packaging strategies to enable *invivo* operation. The realization of biodegradable metal contacts is currently a complimentary research thrust that is being explored in the context of bioresorbable metals for orthopedic and cardiovascular applications.[25, 26] These materials including magnesium based alloys may also find significant utility in development of bioresorbable organic electronic devices.

Concluding Remarks and Outlook

The utilization of biomaterials as structural components in electronic devices has the potential for unique applications in biotechnology and medicine. This newly developing field has only recently begun to explore the interface between biomaterials and organic electronics. Future efforts will likely focus on the expansion of the materials properties through the discovery and characterization of natural biomolecules in addition to the rationale design of synthetic materials including organic semiconductors. Advancements in materials will require parallel breakthroughs in materials processing and fabrication techniques as well. The overall progress of this subject will have widespread implications that span aspects of both fundamental scientific discoveries and technological development. For example, device structures could be fabricated using biomaterials to study fundamentals of electron transfer in naturally occurring semiconducting biomolecules. The investigation of the interface of biomaterials and organic electronics could also lead to the realization of new classes of electronically active bioresorbable medical devices for use in advancing human health. Full realization of this potential can be accelerated by building off of advances in traditional organic electronics, but will ultimately require intimate collaboration across a broad range of disciplines.

Acknowledgments

CJB was funded by an NIH Ralph Kirschstein Fellowship. The authors would also like to acknowledge the work of authors whose work was not able to be featured due to formatting constraints.

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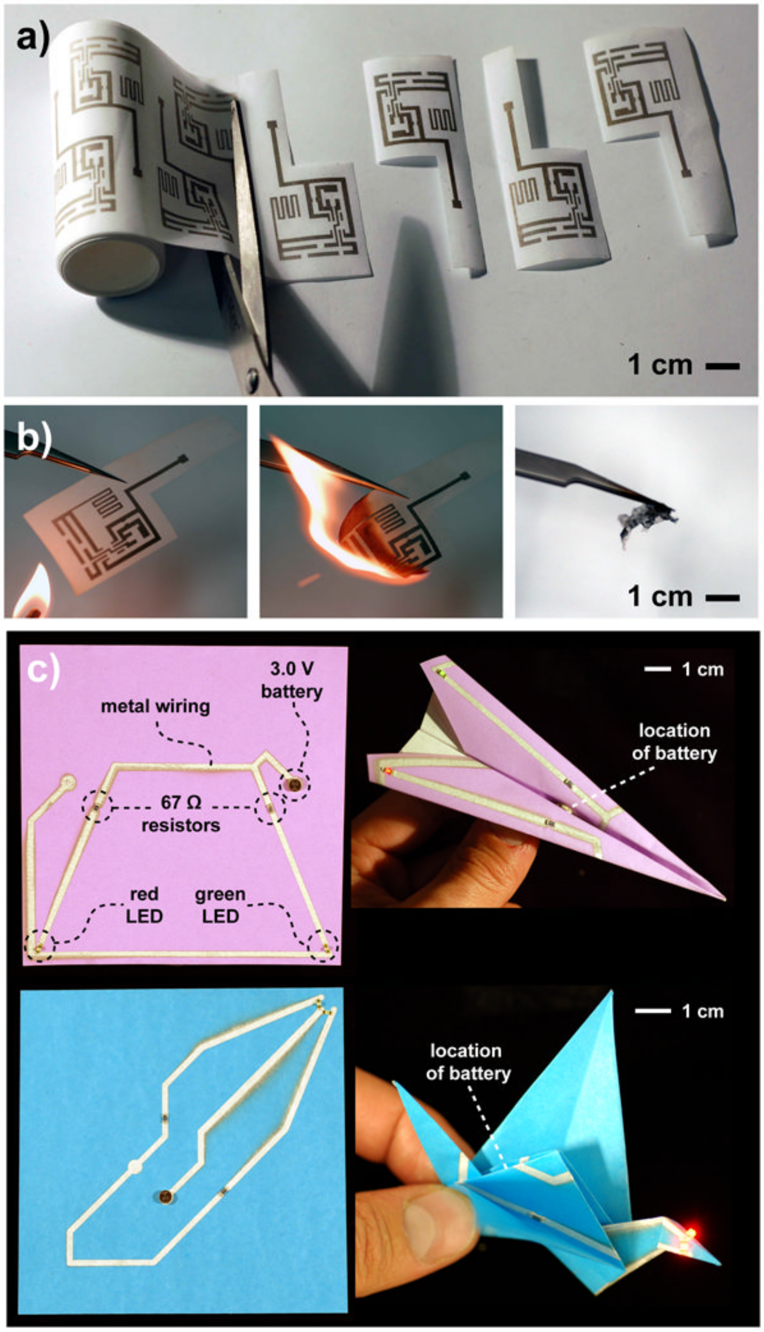

Figure 1. Properties of paper-based electronic circuits

Paper-based circuits demonstrate dramatic improvements in both mechanical flexibility and versatility. (a, b) Trimming and burning fiber-based electronic circuits; in (b), the paper circuit burned in 3 s. (c) Topologically complex electronic circuits on paper demonstrating the ability to form foldable electronic circuits. (above) A paper airplane circuit shown unfolded (left) and folded (right) with battery-powered red/green LED wingtips. The circuit weighs < 1 g and glides like a typical paper airplane. (below) An origami "crane" shown unfolded (left) and folded (right) with battery-powered LED eyes. Electronic traces for both circuits comprised metallic wires (100% In, thickness= 2mm, width = 1 mm, length = 30–

60mm total) patterned on Yasutomo origami paper substrates. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

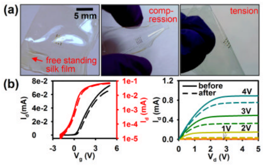

Figure 2. Silicon-Based Devices Fabricated on Bioresorbable Silk fibroin Substrates

Silicon transistors fabricated on silk fibroin substrates maintain adequate device performance after physical bending. (a) Ultrathin devices on a flexible silk substrate, in flat (left) and bent (center and right)configurations. (b) Transfer curves (left) and *I*–*V* curves (right) before (solid curve) and after (dotted curve)dissolution, where I_d, V_g, and V_d represent the drain current, gate voltage, and drain voltage, respectively. The voltage for each *I*–*V* curve in the right frame denotes the gate bias voltage. Silicon devices also demonstrated functionality after silk fibroin dissolution and suitable *in vivo* biocompatibility. Copyright American Institute of Physics. Reproduced with permission.

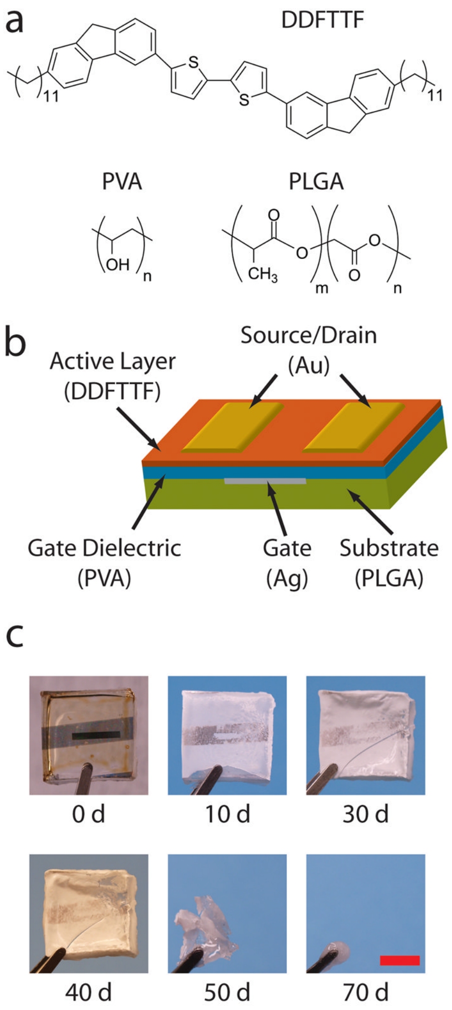

Figure 3. Device Structure and Degradation of Bioresorbable Organic Thin Film Transistors
Materials selection and device configuration of organic thin-film transistors(OTFTs). (a) The chemical structures of the semiconductor (DDFTTF), the dielectric (PVA), and the substrate (PLGA) are shown. (b) These materials are processed into OTFT devices in top-contact configuration as shown. (c) *In vitro* degradation studies suggest that PLGA substrates were initially resistant to mass degradation and water uptake. However, after 30 days, significant mass loss and water uptake was initiated. Near-total mass loss and 100% device hydration was observed at70 days. Photographs from representative devices at various stages of the degradation time line suggest that device integrity was intact up until40 days with near-total device resorption at 70 days. Devices also show a transition from being initially optically transparent (0 days) to opaque within 10 days. Scale bar represents 5mm for all panels. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.