

Flexible Organic Transistors with Natural Materials for Eco-friendly Electronics

A Thesis submitted by
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in partial fulfillment of the requirements for the award of the degree of
Doctor of Philosophy



Indian Institute of Technology Jodhpur
Department of Electrical Engineering
December 2024

Summary and Future Perspective

This thesis explores various approaches to address ongoing issues related to E-waste by utilizing nature-originated materials in device fabrication to develop biodegradable and eco-friendly electronics. Despite the accomplishment of many aspects of eco-friendly electronics through the fabrication of high performance flexible OFETs for sensing and circuit applications, additional developments and advancements are still required to commercialize these organic devices for future biodegradable and implantable applications. This chapter summarizes the key findings with highlighting their potential impact on minimizing e-waste and advancing eco-friendly electronics, along with briefly discussing the comprehensive perspective for advancing this research domain in future.

8.1 SUMMARY

With the increasing awareness of the adverse effects of E-waste on environment and human health, researchers are trying to find alternative technology and materials to develop eco-friendly biodegradable devices for various applications to reduce the carbon footprint of devices after their lifespan. In this regard, natural polymers are being investigated as promising material candidates for device fabrication in this dissertation work, to develop high-performance eco-friendly OFETs. Keeping this in mind, this thesis focused on the utilization of nature originated materials as gate dielectrics along with green processing techniques to demonstrate biodegradable OFETs with excellent electrical and operational stability. To expand the functionality of these devices, sensing, and circuit applications were also demonstrated for different flexible and biodegradable substrates. A widely explored solution-processable semiconductor TIPS-Pentacene and blend of TIPS-Pentacene and PS were utilized to form the active layer due to their easy processability, high mobility and high air stability, so that steady transistor characteristics was obtained in ambient condition. This thesis aims to achieve many aspects including low voltage operation with high stability, multifunctionality, and decomposability of these devices to realize high performance in devices along with their possibility of decomposability in environment. To achieve this, various experiments were performed and following results were obtained:

- I. Selection of suitable nature-originated materials in device fabrication is crucial to balance both eco-friendliness and performance of the devices, as both of these requirements conflict each other. In OFETs, appropriate selection of gate dielectric materials is important to achieve high performance with reliable and stable characteristics for real-world applications. Though the nature-originated materials support the biodegradability and biocompatibility of the devices, it is challenging to use as a single layer gate dielectric due to their inferior dielectric properties including low dielectric constant, high leakage current issues and poor stability under different environment conditions. To avoid these, dielectric engineering like the bilayer of biopolymers was investigated to achieve the optimum results. In some cases, a high- k inorganic gate dielectric was integrated with biopolymer gate dielectric to form the hybrid gate dielectric to reduce the leakage current and support low voltage operation.
- II. Apart from gate dielectrics, semiconductor layer is also crucial to achieve high performance in transistors along with specific applications. High quality dielectric: semiconductor interface is essential for better charge conduction in transistors with low trapping states at the interface. In comparison with the neat TIPS-Pentacene layer, the blend of TIPS-Pentacene and PS was thoroughly investigated to form the active

layer in this thesis along with natural polymers for the enhancement of transistor performance and high electrical stability upon bending and environment through the vertical phase separation between TIPS-Pentacene molecule and PS layer. However, neat TIPS-Pentacene layer was preferred as a photosensitive layer, exhibiting better photo-responsivity, since the charge trapping ability was limited in blend devices under photo-illumination conditions due to lesser interfacial charge densities. In this thesis, the photo-sensing performance of OFETs was specifically investigated towards blue and UV light using TIPS-Pentacene neat layer and natural protein gate dielectric to add eco-friendliness in devices.

- III. Firstly, the suitability of different biocompatible and biodegradable polymers such as PVPy, egg albumen, silk fibroin, chitosan, gelatin, and CEC were comprehensively explored as gate dielectrics along with TIPS-Pentacene or TIPS-Pentacene: PS as active layers. Devices fabricated with a single layer of PVPy, gelatin, and CEC gate dielectric along with TIPS-Pentacene: PS exhibited good transistor characteristics for -5 V operation, showing excellent repeatability, bias-stress stability, and ambient stability. The other biopolymers such as egg albumen, silk-fibroin, and chitosan are difficult to use as a single layer due to their instability and leakage current issues.
- IV. For the demonstration of low voltage operation in OFETs, a pristine layer of gelatin was explored as gate dielectric with TIPS-Pentacene: PS on a flexible ITO-coated PET substrate. The p-channel devices exhibited excellent electrical characteristics for -3 V operation with near zero threshold voltage due to the high-quality dielectric semiconductor interface achieved through optimized processes of using TIPS-Pentacene: PS and ultra-smooth surface of gelatin layer along with the possibility of forming EDL layer due to presence of mobile ions in gelatin solid-state electrolyte. High repeatability, cyclic stability, and high electrical stability upon application of compressive and tensile were achieved for these devices along with very high environmental stability with almost unchanged electrical characteristics over 24 weeks. Further, a resistive load inverter was also implemented, showing good voltage transfer and switching characteristics with these devices to confirm their circuit applicability. These low voltage operated devices are useful for wearable and portable applications for low power consumption.
- V. Further, the multifunctionality was demonstrated in flexible OFETs using bilayer gate dielectric of HfO_2 /gelatin and TIPS-Pentacene as a semiconductor layer. Here, neat TIPS-Pentacene layer exhibited good light sensing capability towards visible and UV light, along with the moisture loving nature of gelatin is suitable for a humidity sensor. Moreover, the pristine gelatin layer with neat TIPS-Pentacene shows high leakage current and variations in transistor performance as compared to blend of polymer semiconductor layer. Thus, a thin HfO_2 layer was integrated by depositing through ALD to enhance the overall dielectric properties by suppressing the leakage current. Moreover, the use of pristine semiconductor layer is crucial for better photo responsivity in OFETs. These devices exhibit excellent electrical characteristics with high field-effect mobility reaching over $2 \text{ cm}^2/\text{Vs}$ (extracted with C_i at 1 kHz), SS of 0.20 V/dec. , and $I_{\text{on}}/I_{\text{off}}$ ratio at a low operating voltage of -5 V. Good light sensitivity for blue and UV light was demonstrated in these devices. Continuous breath rate can be also monitored due to the humidity-sensing capability of gelatin layer, making it suitable for practical applications such as real-time health and environment monitoring. A resistive load inverter was also implemented in these devices. The ability to demonstrate multifunctionality in flexible OFETs with natural protein gate dielectric indicates huge opportunities for development of future smart eco-sustainable systems.

- VI. To utilize the OFET devices in various flexible applications for a long duration, high electrical stability is required for transistor performance upon applications of harsh bending conditions. Pristine gelatin layer has lower mechanical stability due to the deformation and breakage of polymer networks under stress. For the enhancement of stability of device performance under extreme bending conditions, a biopolymer and edible dielectric composite of gelatin and chitosan was investigated as gate dielectric with TIPS-Pentacene: PS layer for the demonstration of flexible OFETs. The formation of strong hydrogen bonding between the ammonium groups of chitosan and the negatively charged side-chain groups in gelatin strengthens the mechanical stability of composite film in comparison to parent films, which is highly dependent on the chitosan quantity. The effect of enhanced properties of this composite was comprehensively investigated on various performance parameters for flexible OFETs for four different gelatin: chitosan ratios of 10:0, 10:1, 10:5, and 10:10. Among all the explored ratios of the dielectric composites, 10:5 exhibited the most superior overall performance compared to others with lowest subthreshold swing value of 0.20 V/decade, low threshold voltage of -0.2 V, high on/off current ratio of 10^4 , and process transconductance value of $14 \text{ nF V}^{-1} \text{ s}^{-1}$, rare to find for flexible transistors with edible gate dielectrics. Devices with 10:5 composition maintained an excellent level of bias-stress stability even after the application of extreme tensile bending for 100 continuous bending cycles. In addition, the 10:5 composite exhibited significantly higher temperature stability than the pristine ones, as confirmed by TGA. Decent switching in inverter circuits and excellent shelf life in ambient for up to 24 weeks were demonstrated in this composite device.
- VII. Further to enhance the biodegradability and reduce the cost of devices, the plastic substrate was replaced by a paper substrate to fabricate flexible OFETs with an already optimized cellulose gate dielectric, both of these materials enhance the eco-friendliness of devices. The cellulose derivative dielectric was utilized as a gate dielectric, offering better mechanical flexibility, chemical and thermal stability as compared to natural protein-based gate dielectric to develop highly stable OFET devices under different conditions. Before fabrication, paper substrate was first planarized by coating a thick PVA layer to suppress the roughness, which is required for uniform thin film deposition.
- VIII. Finally, the optimized CEC dielectric was explored on a biodegradable paper substrate with unique cellulose-based material combinations for the demonstration of decomposable devices. Safe disposability is one of the crucial aspects of minimizing the impact of E-waste on the environment and ecology without producing any hazardous substituents. The EDL effect of CEC gate dielectric at low frequency was confirmed by measuring the gate capacitance density (C_i) for a wide frequency range from 0.1 Hz to 1 MHz, exhibiting a very high C_i value at 0.1 Hz which was about 10 times higher than that obtained value at 1 kHz. Paper OFET devices exhibit good transistor performance for -5 V operation with excellent repeatable transfer curves for 100 continuous scans and excellent bias stress stability with less than 10 % decay for 4600 s. Device performance was comprehensively studied upon exposure to high humidity (RH ~ 80 %) for a total exposure time of 1 hour. For an initial exposure time of 15 minutes, negligible changes of 2.4 % and 6.7 % in I_{on} and SS respectively were observed. However, the degradation in transistor performance was more evident further exposing them for 60 minutes. Initially, improvement in transistor performance was observed due to high ionic conduction supporting the EDL effect, further, the excessive water adsorption degraded the transistor performance due to saturation of polar groups of dielectrics at the dielectric: semiconductor interface. In addition, cyclic stability of devices was investigated in ambient conditions, and in an

extreme humidity environment ($\sim$ RH $\sim$ 100 %). Devices showed excellent switching with $I_{\text{on}}/I_{\text{off}}$ of $\sim 10^3$ during the entire duration of the experiment indicating decent switching stability of fabricated devices before humidity exposure. However, the 'on' current was decayed as expected in the humid environment, though the devices showed high cyclic stability with time. The devices showed quite stable transistor performance upon application of tensile stress for up to 5 mm of bending radius. The effect of annealing temperature on transistor performance was also studied by increasing the temperature from 40 to 100 °C with a step of 20 °C. Initially, up to 60 °C, transistor performance was improved due to the reduction of dipole-dipole interaction in the cellulose-based gate dielectric and increasing the movement of the polar groups. Further, the increment of annealing temperature deteriorated the transistor performance due to the loss of ionic conductivity and generation of cracks in the semiconductor crystals along with defects in the dielectric: semiconductor interface. The decomposability of these paper devices was successfully investigated by immersing them in water-rich soil at room temperature. The mechanical strength of the cellulose network of the paper substrate was degraded by water molecules. Moreover, the fungi and bacteria present in the soil degraded the paper substrate quality and other organic materials within 3 weeks, confirming their suitability for biodegradable electronics. The overall good performance of the OFETs with CEC gate dielectric on paper substrate makes these devices excellent candidates for further exploration for future biodegradable and eco-friendly electronics.

8.2 CONCLUSION

After analyzing the several findings in this thesis, it can be concluded that the natural polymers exhibit promising dielectric properties for the demonstration of high performance eco-OFETs on various flexible and biodegradable substrates. The suitable selection of these materials along with proper dielectric engineering and OSCs enhanced the overall transistor performance. Low voltage operated flexible eco-friendly OFETs were demonstrated for diverse applications like light and humidity sensing along with circuit applicability. Further, fully degradable OFETs on biodegradable substrate were demonstrated for future eco-sustainable electronics. A widely explored promising organic semiconductor TIPS-Pentacene and polymer blend of TIPS-Pentacene: PS were utilized to form the active layer, depending on their specific requirements. Neat TIPS-Pentacene layer was used for light sensing, on the other hand, TIPS-Pentacene: PS was preferred for better transistor performance and electrical stability. This dissertation starts with exploration of various biocompatible and natural polymers to investigate their suitability as gate dielectric in transistors as discussed in Chapter 3. To utilize the OFETs in wearable and portable applications, low-voltage operation was achieved using gelatin gate dielectric and TIPS-Pentacene: PS on ITO-coated PET substrate. Excellent electrical, operational, and environmental stability were obtained in these devices, and results are discussed in Chapter 4. Further to enable the multifunctionality in OFETs, a bilayer gate dielectric of HfO_2 /gelatin with TIPS-Pentacene photosensitive active layer was demonstrated, exhibiting good transistor performance and good sensitivity towards blue and UV light, relative humidity and real time breath rate monitoring, as discussed in Chapter 5. The electrical and operational stability upon application of continuous bending was enhanced by exploring a biopolymer composite of gelatin and chitosan with TIPS-Pentacene: PS for a flexible substrate. The results are discussed in Chapter 6, showing excellent transistor performance for 100 continuous bending cycles along with environmental stability for up to 24 weeks. Cellulose derivative dielectric cyanoethyl cellulose was utilized as gate dielectric in OFETs since it has high thermal stability, flexibility, and moisture resistance in comparison with gelatin natural protein. A fully decomposable device was demonstrated on paper substrate using CEC dielectric, exhibiting high performance and excellent stability under different conditions as discussed in Chapter 7. Transistor performance under extreme humid environment (RH $\sim$ 100 %) and on increasing the annealing temperature with upon application of bending and bias-stress were briefly discussed. Finally, paper devices were successfully decomposed in soil, confirming their excellent biodegradability.

8.3 FUTURE PERSPECTIVE

The primary focus of the dissertation was to demonstrate low voltage operated eco-friendly OFETs for multi-parameter sensing and circuit applications, along with complete decomposability in nature. Although the primary aims of this thesis have been accomplished, there is still a possibility of expanding this work in the future. Some of the potential future perspectives are discussed as follows:

- I. The transistor performance can be enhanced by investigating other potential small molecule and conjugate polymer semiconductors as channel layer with high carrier mobility and air stability. Utilizing another semiconductor with better photo-sensing property than TIPS-Pentacene will enhance the light sensitivity of the OFETs.
- II. Though paper was used as a biodegradable substrate, the high surface roughness with low mechanical stability limits the transistor performance on paper substrate. Utilizing other natural polymers such as gelatin, silk-fibroin, and chitosan, as alternative biodegradable substrates with better surface morphology and flexibility, will improve the performance of the transistors. In this regard, proper substrate preparation methods should be explored with accurate material quantity, solvent, and annealing temperature to obtain a suitable biodegradable substrate.
- III. Apart from dielectrics and substrates, future work can focus on the exploration of new and novel nature-inspired organic semiconductors and cellulose-derived conductive electrodes to fabricate an OFET device by adding eco-friendliness in all material candidates. This work is still limited at device level; further advancement can be done both in design and processing levels to develop biodegradable systems for different applications.
- IV. Despite the promising potential of eco-friendly electronic devices, several key challenges must be addressed for large-scale commercial production. A major bottleneck lies in the incompatibility of natural and biodegradable materials with conventional high-throughput fabrication processes, which limits scalability. To overcome these, future research must focus on optimizing the synthesis and processing of sustainable materials to achieve uniformity, developing cost-effective and scalable fabrication techniques compatible with flexible substrates. Strong collaborations between academia and industry will be key to accelerating the transition of eco-friendly electronics from laboratory prototypes to commercially viable products.