

Chapter 8

Biocompatible Integration of Electronics Into Food Sensors

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Chapter Outline

1. Introduction	247	4.2 Semiconducting Materials	256
2. Bioelectronics	248	4.3 Dielectric Materials	257
3. Sensors and Biosensors for Food Industry	251	4.4 Field-Effect Transistors for Food Control Applications	259
4. Materials	253	4.5 Conclusions	267
4.1 Substrates for Bioelectronics	254	References	268

1. INTRODUCTION

We live in a society dominated by technology and electronic devices. We communicate or book our holidays using smart phones; read the news on our ultralight touch screen tablets or order gifts for our loved ones with a simple click of a mouse. Technology is part of our daily routine and has positively impacted all economical sectors. It has also changed the way we communicate and socialize.

But 100 years ago, all these would have seemed drawn from a science fiction novel. When Julius Edgar Lilienfeld predicted and described the field-effect transistor (FET) [1], more than 90 years ago, he did not foresee that this laboratory curiosity would radically change and reshape our society. Other 34 years had to pass till Dawon Kahng and Martin Atalla realized the first metal-oxide-semiconductor field-effect transistor (MOSFET) [2]. Few years after, the device was commercially available. Nowadays almost every electronic device has a MOSFET integrated. The most common semiconductor

used is highly doped crystalline silicone, which is also the substrate of the circuit. Without a doubt the main beneficiary of this advancement is the IT industry. In the last decade, computers and laptops have become more affordable, lighter and high performing mainly due to the impressive development made in this field, allowing millions of transistors to be integrated and miniaturized on the same chip as predicted by Moore's Law [3].

Thin-film transistors (TFTs) are electronic devices based on the FET principle, where the semiconductor is deposited as a thin film on an insulating substrate such as glass, metallic oxides or plastic substrates. Traditional inorganic TFTs are based on amorphous silicon (a-Si:H) or polysilicon. The first organic transistor was fabricated and tested in the late 1980s, having an electrolyte as gating medium. This transistor was not a pure FET but rather an electrochemical transistor (ECT). In 1986, the first device showing clear transistor behaviour was made and tested successfully by Tsumura et al. [4]. The story behind organic thin-film transistors (OTFTs) starts in the late 1970s when Heeger, Shirakawa and MacDiarmid obtained a novel conductive polymer by doping polyacetylene with arsenic iodine, chlorine and bromine [5]. This was considered the starting point of a new era – conductive polymers. For this crucial discovery, in 2000, they were awarded with the Nobel Prize for Chemistry. Since then, organic semiconductor (OSC) materials have been intensively studied and upgraded (in terms of electrical performance) thanks to the enormous research done in the field of organic chemistry, leading to the synthesis of new solution-processed molecules such as oligo and polythiophenes [6]. These efforts were the origin for a completely new technological field, based on the properties of conductive organic materials. 'Plastics' that can exhibit electrical properties comparable to those of silicon-based semiconductors have opened up the possibility of making a large range of electronic devices that can be thin, flexible and eventually completely disposable such as organic light-emitting diodes (OLEDs), OTFTs and solar cells.

In addition, OSCs have proved to be among the best candidates to be interfaced to many biological molecules [7,8] due to many other properties such as synthesis, tunability, processing, softness and self-assembling ability. Their better mechanical compatibility with tissue than traditional 'hard' electronic materials and improved biocompatibility [9,10] with mechanically flexible substrates well suits the nonplanar form factors often required for medical implants [11].

2. BIOELECTRONICS

Without a doubt, electronics and microelectronics have completely reshaped research areas such as medicine and biology. Thanks to this 'symbiosis', between biology and electronics that gave birth to 'bioelectronics', scientists have now a whole new range of analytical tools currently used in medical

diagnosis, novel drugs discovery, food safety, environmental monitoring and national security.

In biology, for example, characterizing biological systems at a molecular and cellular level is possible thanks to the existing available techniques: optical and fluorescence microscopy, DNA and protein analysis or Patch clamps [12].

But also sensors, or more specifically biosensors, can be designed when surface chemistry is used as a bridge between biological molecules and electronics transducing devices. The biomolecule in contact with its complementary molecule (analyte) will produce a specific effect measured by the transducer, which converts the information into a measurable effect, eg, electrical signal as depicted in Fig. 1.

The first enzymatic biosensor [13] was proposed by Clark and Lyons more than 50 years ago. Since then many types of biosensors have been developed interfaced with all kind of bio-receptors: antibody/antigen interactions, DNA and ARN interactions, enzymes and cellular interactions and even interactions due to synthetic bio-receptors. Depending on the physicochemical properties of the interest analyte, optical, electrochemical or mass-sensitive transducers can be used.

Antibody-based biosensors are the most specific and reliable sensing devices exploiting the unique lock and key fit property of antibodies, meaning that the specific geometrical configuration of the antibody (unique key) enables it to open a specific lock (antigene).

By using radioactive-marked antibodies (radioimmunoassay), scientists have been able to detect specific analytes where other analytical techniques have been failed. Pharmacology, clinical chemistry, forensics, environmental monitoring and food safety are just few of the fields where this analytical method can be applied to. However, the use of highly unstable, potential dangerous radioactive materials plus the high overall costs are limiting factors for using this method. Research groups all around the world have dedicated

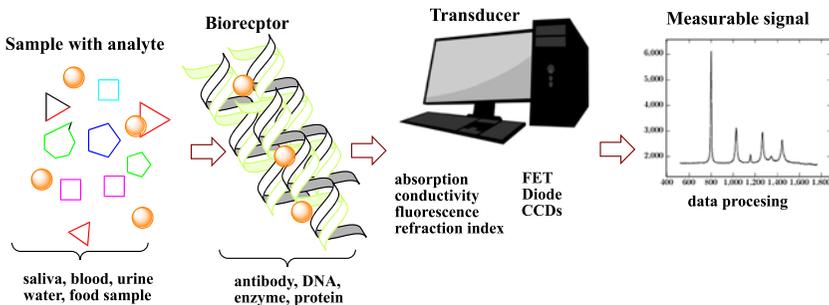


FIGURE 1 Schematic representation of a biosensor. *FET*, Field-effect transistor.

their efforts to develop new, simpler and practical immunochemical instrumentation techniques comparable to the high sensitivity and selectivity of radioimmunoassay. Advances in device miniaturization, biotechnology and nanotechnology have allowed fabrication of antibody-based biosensors capable of detecting analytes of interest inside a single cell [14]. Such nano-scale devices were used for optical detection of benzo[a]pyrene metabolites when a specific monoclonal antibody was used as a bio-receptor. This method permits cellular probing for both analyte detection [15] and cell signal monitoring.

Enzymes also can be used as bio-receptors and have both specific binding and catalytic capabilities. In this case the bio-detection is amplified by a reaction catalysed by the biocatalyst. The catalytic activity of enzymes allows reaching lower limits of detection as compared to the common binding techniques. However, this extra boost in method sensitivity is strictly related to the integrity of the native protein conformation. The enzyme will become catalytic inactive if it is denatured or broken down into subunits. Both the enzymes and the bioaffinity biosensors were originally found and used mainly in labs or hospitals. But now, thanks to the advances made in the field of easy-to-use bioelectronics, portable devices for non-specialists (eg, glucose meters or pregnancy tests) are available in pharmacies or even in supermarkets.

Another type of biosensors uses nucleic acids as bio-receptors allowing the detection of DNA or RNA in human samples. A labeled complementary sequence is added to the samples after the unwinding of the DNA double helix into single strands. If the sequence of bases of the target analyte (eg, virus or bacteria) is known, the labeled probe will hybridize to its complementary sequence, giving rise to a fluorescent signal that is then transmitted to a signal generator.

Microorganisms can also be employed as bio-receptors interfaced with electronic devices. Bacteria, fungi or even viruses are extremely sensitive and can be successfully used as indicators of toxicity for various chemical substances. These biosensors usually offer extremely low detection limits due to signal amplification. This is mainly due to the complex biochemical structure of the microorganism and their catalytic properties.

But also man-made or artificial receptors can be used to fabricate biosensors, thanks to the advances made in the field of genetic engineering and molecular imprinting. By using these techniques, scientists are able to alter clones and genes of an organism to produce new biological substances such as membranes, proteins or hormones. Molecular polymer stamps can be designed when the analyte molecules are mixed with monomers and cross-linkers. After polymerization, the analyte molecules are removed from the polymer network. The final polymer structure will have molecular binding sites complementary to the interest analyte. These molecular imprinted polymers can withstand harsh environments such as temperature or chemicals that would normally denature a protein, thus making them extremely attractive. However, these

biomimetic receptors exhibit lower selectivity as compared with their natural receptors.

The next section will discuss how sensors and biosensors can be used in quality control for food safety applications.

3. SENSORS AND BIOSENSORS FOR FOOD INDUSTRY

Within the last decades the food industry has experienced an impressive growth both in terms of the amount of foodstuff produced and sold and in terms of product quality. Food products have been created to meet our daily lifestyles and new eating habits. The perishable nature of food products along with a stiff competition has forced the food industry to rapidly adapt and comply with the increasingly stringent worldwide food regulations. In the same time the food companies have realized the financial benefits deriving from a better quality control and quality assurance concerning foodstuff production. Safe, high quality and easy traceable products translate into lower costs, higher market share and customer satisfaction.

New lines for intelligent manufacturing, packaging and food quality control have been developed to increase the shelf-life while maintaining the product quality. New equipments and technologies for processing and packaging technologies incorporating sensing platforms, identification tags such radio frequency identification, automated sampling and imaging systems were specially designed for the food industry.

Released gasses, flavored compounds, volatile molecules or chemical-specific species associated with food freshness or ripening stages can be qualitatively and quantitatively detected using many chromatographic techniques. Near-infrared spectroscopy such as FTIR (Fourier transform spectroscopy) is extremely attractive for surface analysis allowing simultaneous identification of different chemical compounds.

Even though these traditional analytical techniques are extremely robust, reliable and offer good reproducibility, the main drawback is that they cannot be integrated in the production or packaging flow, which in many cases is critical. Other handicaps include expensive instrumentation, time-consuming analysis or well-trained personnel. For these reasons, (bio)sensing online platforms can become an extremely attractive alternative to traditional techniques. If properly designed, these platforms could be fully integrated either in the manufacturing flow or directly in/onto the foodstuff package providing a good traceability of the product as well as guaranteeing the product quality.

Various types of sensors (physical, chemical, biological) have been developed that allow food quality monitoring. Food freshness [16], pathogens detection [17], carbon dioxide [18] and oxygen [19] concentration, pH [20] and temperature [21] can be monitored using these devices.

Smart or intelligent packaging is the new trend in food industry that allows incorporation of such sensors into the food packaging technology. This

technology is able to prolong shelf time and protect food from environmental contaminants and allows online quality control information and traceability of the product. In other words, this packing technology can sense the environment inside or outside the package and provide information to the producer, consumer or retailer about product parameters. Generally speaking, this term can also refer to product identity, authenticity and traceability.

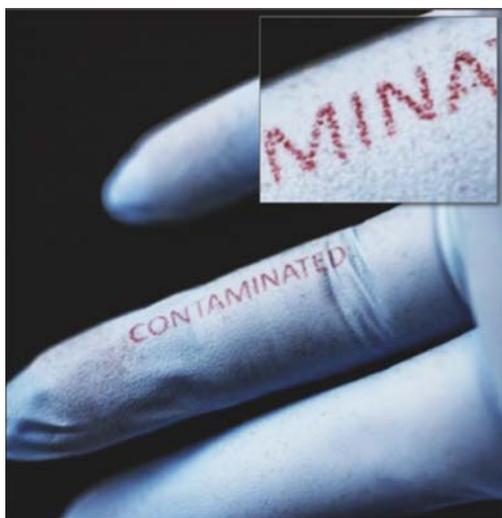
Smart labels and sticker [22] are already used to provide consumers with simple and reliable information regarding product ingredients and how the product should be used. But smart labels include also time-temperature indicators [23] that can reveal changes in the colour or shape of the product.

For example, Omenetto et al. developed different silk-based solutions that can be mixed with enzymes, antibiotics, growth factors or antibodies. These functional inks [24] were then used and printed on different substrates. As a proof-of-principles, the authors printed a pattern on a surgical glove, Fig. 2, that changes colour when exposed to bacteria. This technique could be used for large-scale fabrication of smart food packaging foils patterned with functional inks, for different contaminant's detection.

Many companies, universities, and research institutes are directly involved in this field by developing biosensor devices or novel biosensing techniques that are/could be used in smart food packaging.

Enzymatic-based biosensors for pesticide [25] detection or label-free immunochemical sensors for antibiotics screening in milk [26] were developed in Higson's group. An electrochemical sensor designed for the detection of polyphenols in olive oil [27] or a disposable electrochemical DNA array for hazelnut allergens detection [28] were also successfully developed in

FIGURE 2 Surgical gloves with printed patterns turning to red, showing 'CONTAMINATED', after exposure to *Escherichia coli* at a concentration of $\approx 10^4$ CFU/mL, indicating contamination. From H. Tao, B. Marelli, M. Yang, B. An, M.S. Onses, J.A. Rogers, et al. *Adv. Mater.* 27 (2015) 4273–4279. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.



Mascini's group. Electrochemical biosensors for the detection of mycotoxins such as Aflatoxin M1 in milk [29] or Ocharatoxin A [30] were proposed by Marty's group. The latter group is also involved in developing enzyme-based sensors for the detection of organophosphorus pesticides [31].

Other biosensors development by universities for food safety analysis includes antibiotics [26,32] detection (in food and milk), bacteria (eg, *Escherichia coli* or *Salmonella*) [33,34], herbicides and pesticides (in milk or fruit juice) [35,36], ethanol [37], aldehydes [38] and catechol [39] in alcoholic beverages, amines in fish [40], fruits and vegetables [41], oxalates [42] and sulphites [43].

Unfortunately, not all of the biosensor prototypes developed by academia are commercially available. R&D companies such as Neogen Corporation (www.neogen.com) or Roche Diagnostics AG (www.roche-diagnostics.com) provide clients in the food industry, with rapid-screening solution for food quality control applications.

The Food Safety Division of Neogen offers kits and ready-to-use screening tools for foodborne bacteria, spoilage organisms, mycotoxins, food allergens, genetic modifications and drug residues. The company also commercializes an extremely simple dipstick test that detects dairy antibiotics in the beta-lactam group, requiring only minimal training and equipment. The Listeria Genus Detection Kit from Roche detects rapidly Listeria DNA that is isolated from cultures inoculated with food sample material. The presence of the pathogenic species *Listeria monocytogenes* in positive samples might be further confirmed by using other detection kits. This detection kit is rapid, highly sensitive with specific response and also minimizes the risk of sample contamination and false-positive as well as false-negative results.

Other commercially available biosensors for food industry include glucose, ethanol and methanol sensors (Biometra Biomedizinische Analytik GmbH, Germany), glucose and lactate (Solea-Tacussel, France), fish freshness (Oriental Electric, Japan) and bacteria (Sweedish BIACORE AB/Sweden, Malthus Instruments/United Kingdom, Biosensori SpA/Italy, Biotrace/United Kingdom).

Ideally, these sensors should be fully disposable and have a minimum environmental impact. However, finding biocompatible or biodegradable materials for interfacing electronics with enzymes, antibodies or proteins is still a big challenge. For this reason, in the next section we will present a highlight of the state-of-the-art reports for organic electronics applications involving biocompatible, biodegradable, natural-like and easy tunable materials.

4. MATERIALS

Biological materials or bio-inspired materials are usually regarded as niche materials used in specific areas, such as medicine, medical engineering,

biotechnology, or for pharmaceutical applications. Biological materials are present in living organisms or produced by them and do not contain any synthetic substances and are biodegradable. Biomaterial or a bio-inspired material is a mixture of synthetic and natural substances that can be easily interfaced with living cells, tissues or organs. If this interfacing does not produce any immune reaction, the material is regarded as biocompatible.

To be biocompatible, biological materials must have low or no toxicity or cytotoxicity (cell killing ability).

4.1 Substrates for Bioelectronics

Edible polymers can be used for food wrapping [44], packaging [45] or as physical support for biosensing devices [46]. Human or animals can safely consume these materials without any harmful effects to the health. They degrade more rapidly than their synthetic counterparts, making them viable solutions to the huge amount of non-biodegradable plastic wastes generated currently by the food packaging industry.

Edible polymers are usually used as coating layers to protect food products against the loss of nutrients. But can be used also as implantable bioresorbable scaffolds for bone surgery [47] or polymer–anticancer drug conjugates [48].

There are four categories of edible polymers:

- A.** Hydrocolloids: cellulose derivatives, collagen, chitosan, gelatine, starch, soy protein, lentil protein, whey protein, peanut protein, Mung Bean;
- B.** Polypeptide: zein, casein and whey proteins, gluten and soy proteins;
- C.** Lipids: carnauba wax, beeswax, candelilla wax and shellac;
- D.** Synthetic and composite edible polymers: lipids and hydroxypropyl methylcellulose, methylcellulose and lipid, methylcellulose and fatty acids, corn zein, methylcellulose and fatty acid, gelatin and fatty acid, soy protein isolates and gelatin and soy protein isolate and polylactic acid, polyvinyl acetate, polymethyl methacrylate (PMMA).

But also paper [49–52], leather, silk [24,46] or other polymers [54] can be used as biodegradable substrates for bioelectronics [53].

Paper is a versatile material and produced by mixing cellulose fibres together with additives, clays and dyes. Flexible paper sheets are obtained after pressing and drying the cellulose-based mixture. Paper is used for writing, printing, packaging, cleaning and also as substrate for fabrication of electronic circuits (Fig. 3) due to its low cost, versatility and biodegradable properties. Recent reports have demonstrated that even solar cell devices can be integrated on paper substrates [52]. By incorporating state-of-the-art polymers and electrode materials, the authors reported 4% efficiency for these paper-based solar cells.

Pentacene-based OTFTs and ring oscillators were developed by Eder and his group, on commercially available paper [49]. The transistors exhibit carrier



FIGURE 3 (Left) 4% efficient organic solar cells fabricated on paper substrates with a zinc coating acting as the back contact and evaporated MoO₃/Ag/MoO₃ semitransparent top electrodes. (From L. Leonat, M.S. White, E.D. Głowacki, M.C. Scharber, T. Zillger, J. Rühling, et al. *J. Phys. Chem. C*. 118 (2014) 16813–16817. Copyright American Chemical Society Reproduced with permission.) (Right) Organic field-effect transistors (OFETs) and integrated circuits on paper substrates. (From F. Eder, H. Klauk, M. Halik, U. Zschieschang, G. Schmid, C. Dehm, *Appl. Phys. Lett.* 84 (2004) 2673. Copyright American Institute of Physics. Reproduced with permission. Colour image courtesy of Hagen Klauk.)

mobility of 0.3 cm²/V and a current on/off ratio of 10⁶, similar to the results reported for pentacene TFTs on PEN films.

Polysaccharide circuit boards (PCBs) were developed and characterized by using laminate composite nanocellulose thin films on water-soluble sugar substrates as a bilayer [55]. Conductive pads and tracks were afterwards defined onto the PCB by means of conventional evaporation and printing techniques. A simple light-emitted circuit (light-emitting diode, LED) was developed on a PCB, as showed in Fig. 4C and transferred on a petal flower. Even though the luminescence was lower after the transfer, no cracking or mechanical wear was observed during operation.

Organic field-effect transistors (OFETs) were successfully designed and tested by Irimia-Vladu et al. using hard gelatine [10] as a biocompatible and biodegradable substrate (Fig. 4, right). Gelatine is mass-produced from collagen by processing animal skin, tissues and bones. The food and pharmaceutical industries use important quantities of gelatine for the production of jams, gummy bears, as drug excipient or hard gelatine capsules for drugs.

Edible food sensors [46] based on wireless passive antenna technology were developed and integrated on silk substrates in Omenetto's group. The sensors, operated at different frequency regions, were conformably attached to fruits or cheese, and the spoilage process was monitored. As a proof-of-principle, the resonant frequency response of these sensors attached to foodstuff was measured, and ripening of bananas and spoilage of cheese could be monitored, as depicted in Fig. 5.

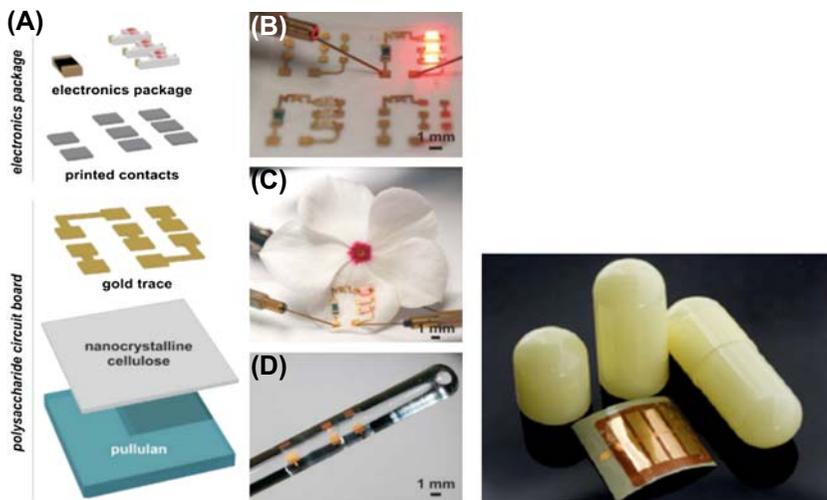


FIGURE 4 (Left) (A) Schematic of a typical electronic decal fabricated on a polysaccharide circuit board, in which the dissolution of the water-soluble pullulan substrate results in a conformal electronic device with nanofibril cellulose substrate. (B) Operation of the PCB-LED circuits on a full-sheet. (C) The PCB-LED circuit was excised and transferred to a biological surface. (D) A polysaccharide circuit board laminated around a glass rod to illustrate flexibility and transparency. (From M.A. Daniele, A.J. Knight, S.A. Roberts, K. Radom, J.S. Erickson, *Adv. Mater.* (2015) 1–7. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.) (Right) Organic field-effect transistors fabricated on edible hard gelatin capsule. (From M. Irimia-Vladu, P.A. Troshin, M. Reisinger, L. Shmygleva, Y. Kanbur, G. Schwabegger, et al. *Adv. Funct. Mater.* 20 (2010) 4069–4076. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

These are just few examples of how unconventional materials can be successfully used for developing new sustainable sensors and devices.

4.2 Semiconducting Materials

The field of ‘solution-processed semiconductors’ is huge, and hundreds of companies and universities are developing every day new organic and inorganic molecules with semiconducting properties. These materials are not fully compatible with bio-interfaces or with bio-molecules, have a high cost and degrade rapidly when exposed to air. There are, however, some exceptions since naturally or naturally inspired compounds can be used as semiconductors for bioelectronics fabrication.

OFETs, OLEDs or organic solar cells can be fabricated using natural semiconductors, used since ancient times, such as indigo, a pigment extracted from plants [56,57] or tyrian purple which was originally extracted from sea snails [58,59]. These two materials as well as other ‘nature-inspired’ indigoids exhibit good ambipolar properties. Molecular structure of indigo, epindolidione and quinacridone, as well as the colour of these compounds in solution, is presented in Fig. 6.

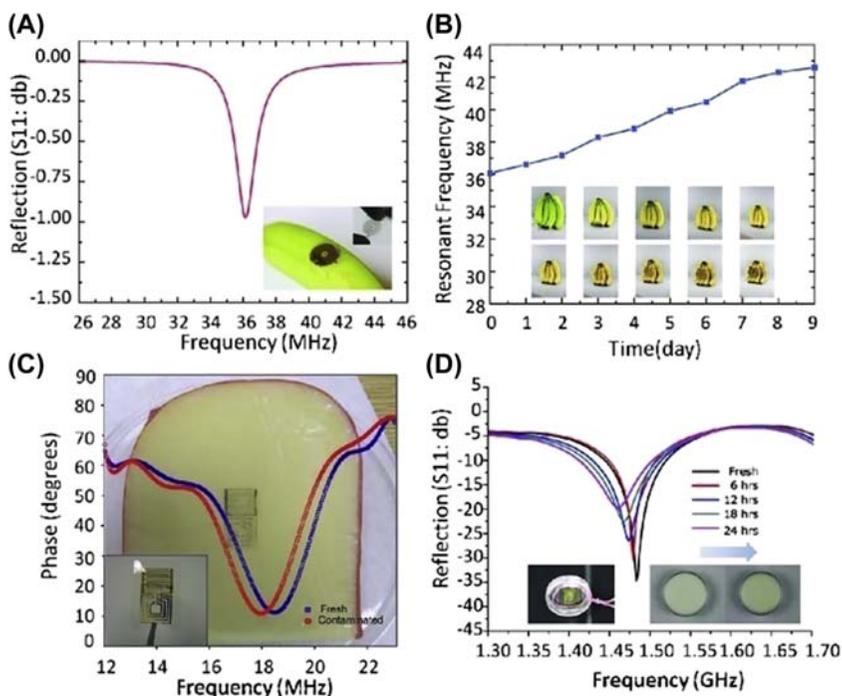


FIGURE 5 (A) Reflection spectra of a silk radio frequency identification-like antenna attached to a banana. (B) Measured time-dependent resonant frequencies of the silk antenna measuring a ripening banana over a 9-day period. (C) Measured frequency-dependent impedance phase angle of a silk sensor applied to a slice of cheese (*blue curve* (dark grey in print versions)) to detect bacterial contamination (*red curve* (dark grey in print versions)). (D) Measured frequency responses of a silk sensor for a milk spoilage detection. From H. Tao, M.A. Brenckle, M. Yang, J. Zhang, M. Liu, S.M. Siebert, et al. *Adv. Mater.* 24 (2012) 1067–1072. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Good electronic performances were reported for epindolidione-based low-voltage FETs (Fig. 7). These devices exhibited hole mobilities of $0.05\text{--}1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ and electron mobilities up to $0.1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ [60]. Also, these materials are extremely stable in a wide range of electrolyte solutions and show no observable degradation after hundreds of cycles of operation. These findings demonstrate the potential of using such highly stable pigments as versatile organic semiconducting materials. But even oligo-olefins such as carotenoids can be used as natural semiconductors, although the mobilities values ($1 \times 10^{-4}\text{ V}^{-1}\text{ s}^{-1}$) obtained for these materials are much lower compared to indigoids or epindolidiones [60].

4.3 Dielectric Materials

Nature provides also an impressive number of biodegradable and biocompatible materials with dielectric or insulating properties. DNA, for example, is

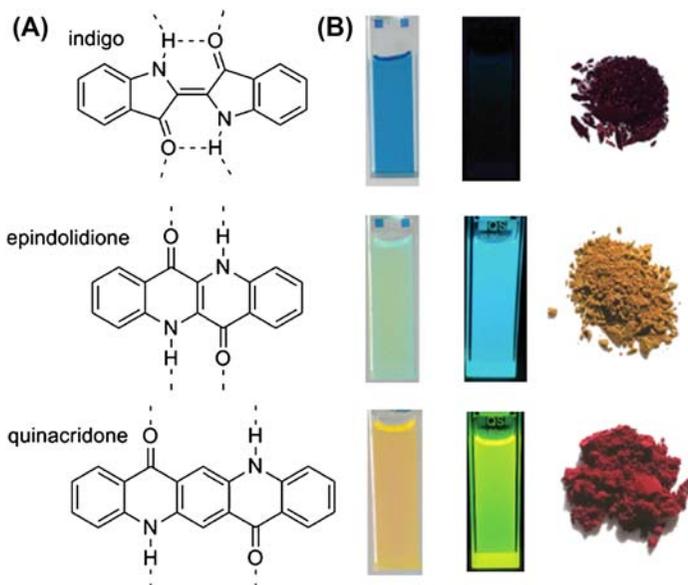


FIGURE 6 (A) Molecular structures of indigo, epindolidione and quinacridone. (B) Solutions of each material in dimethyl sulphoxide (DMSO), with photoluminescence excited at 365 nm. *E.D. Głowacki, G. Romanazzi, C. Yumusak, H. Coskun, U. Monkowius, G. Voss, et al. Adv. Funct. Mater. (2014) 1–12. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.*

mainly known for its encoding properties, but this versatile molecule was also used and successfully employed as functional layer in organic electronics [7,61–63].

Electron blocking layers for OLEDs were formed by spin-casting-modified DNA polar solutions. The luminance and luminous performance of these DNA-based LEDs were 10 times higher than those of LEDs using common polymers [63].

Gate dielectrics based on DNA were also successfully used for fabricating OFETs [7]. However, high hysteresis is a major drawback of these devices, most probably due to mobile ionic contaminants present in the dielectric layer. This problem can be solved by incorporating additional blocking layers to the FET structure (such as metal oxides) or by using cross-linkers. Irimia-Vladu et al. demonstrated that also adenine, guanine, thymine and cytosine (DNA sequence bases) could be used as gate dielectric for OFETs [9]. These vacuum-processed nucleobase-based OFETs exhibited good electrical performances and showed minimal or no hysteresis in the transfer characteristics.

Investigations revealed that comparable dielectric constants [64], to that of polyvinyl alcohol (PVA), can be achieved when using solution-processed sucrose, glucose and lactose-based dielectric layers.

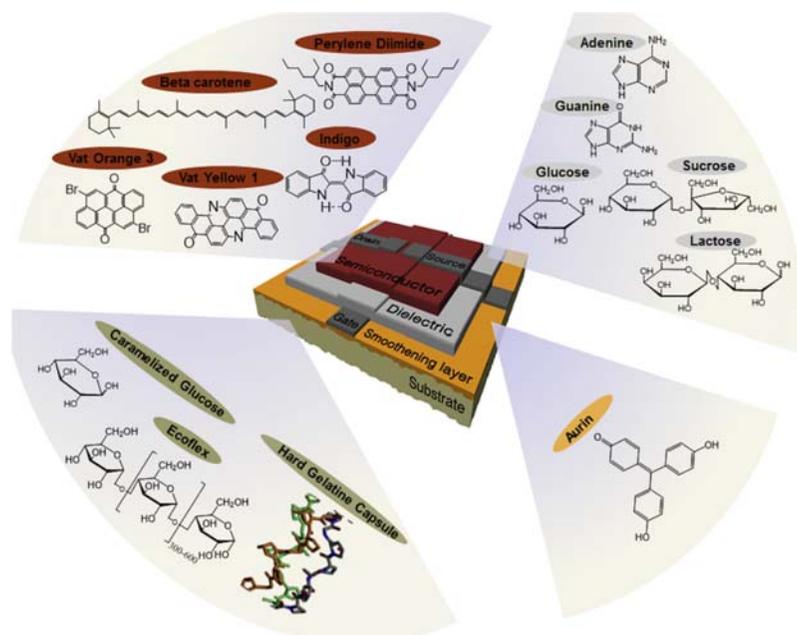


FIGURE 7 An organic field-effect transistor constructed using only natural materials or materials inspired by nature. Hard gelatine or starch-based foils such as Ecoflex were used as substrates; while natural aurin was used as a smoothing layer. Natural ‘sweet’ dielectrics such as glucose, fructose and sucrose can be used as insulating materials. Both natural semiconductor such as indigo and β -carotene can be used as semiconductors inspired by nature. *From M. Irimia-Vladu, P.A. Troshin, M. Reisinger, L. Shmygleva, Y. Kanbur, G. Schwabegger, et al. Adv. Funct. Mater. 20 (2010) 4069–4076. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.*

4.4 Field-Effect Transistors for Food Control Applications

From flexible displays [65] to disposable sensors [66], cyborg roses [67], TFTs and FETs have attracted a lot of attention in the recent decades, mainly because of the diverse areas in which these devices find application.

This last section aims to provide readers with an overview of some high-profile scientific articles and findings reporting sensing applications in which TFTs and FETs were used as transducers.

TFTs are three-terminal devices consisting of a thin semiconductor layer, a gating medium (insulating/dielectric layer) and three conductive terminals, called source, drain and gate electrodes. Source and drain are in direct contact with the semiconductor layer (organic or inorganic) and separated by a short distance, thus forming a semiconducting channel. The third contact, the gate, is separated from the semiconductor by a gate medium. Upon the application of a source-drain voltage (V_{DS}), a current (I_{DS}) may flow in the semiconducting

channel. The magnitude of the I_{DS} is modulated by a voltage applied to the gate electrode (V_{GS}), which generates an electric field perpendicular to the channel and thus may attract mobile charges carriers into it. In addition to the manifold applications of OFETs in electronics, these devices have attracted interest as transducers for sensing applications. Thanks to gating, OFETs may display much higher currents (I_{DS}) than simple (ungated) organic chemiresistors, where low current may lead to poor signal/noise ratio. Also, multiple independent parameters can be extracted from the single characteristics of a single transistor, thus providing rich sensor information. Interest in OFET sensors has multiplied through the recent introduction of electrolytes, instead of dielectrics, as gate media. These were initially introduced for their high capacitance, leading to low operational voltages. However, since electrolytes are ubiquitous in life- and environmental sciences, the 'EGOFET' (electrolyte-gated organic field-effect transistor) opens up manifold possibilities for novel bio- and environmental sensors. In this section we will focus only on the OFETs and EGOFETs as transducers for gas and liquid sensing applications.

In the case of OFETs, charges can be induced at the insulator–semiconductor interface, when a gate voltage is applied. Electrons or negative charges will be induced in the semiconductor layer upon applying a positive gate voltage, while a negative voltage will induce holes or positive charge holes. These charges (holes or electrons) will increase the conductivity of the semiconductor, and a conducting channel will be formed between the source and drain electrodes. A positively charged channel is called *p*-channel, and a negatively charged channel is called *n*-channel. By varying the gate voltage, the channel conductance can be modulated.

EGOFET device mechanism is based on the formation of nanometric scale electrical double layers (EDLs) at the gate–electrolyte interface and electrolyte–semiconductor interface, respectively. The high capacitance of electrolytes ($\approx \mu\text{F}/\text{cm}^2$ range) allows EGOFETs operation at a sub-volt regime.

The FETs are excellent candidates for sensing applications mainly because these devices are capable of current amplification, and changes in the transport properties can be measured upon exposure to a gas, for example. These devices can be used as multi-parameter sensors by monitoring simultaneously the variation of mobility (μ), current *on/off* ratio, threshold voltage (V_T) and bulk conductivity in the semiconductor layer. Torsi et al. proposed this model for the first time in the year 2000, for an OFET sensor exposed to a gaseous analyte [68].

The same group demonstrated that high sensitivity and selectivity can be achieved when using an alkoxyphenylene–thiophene bilayer semiconductor for making an OFET-based sensor, Fig. 8 [69]. The proposed gas sensor was able of chiral discrimination between (S)- β -citronellol and (R)- β -citronellol as well as to 'sense' the racemic mixture.

Four years after these findings, Angione et al. proposed an OFET gas sensor incorporating a functional bio-receptor, the so-called FBI configuration

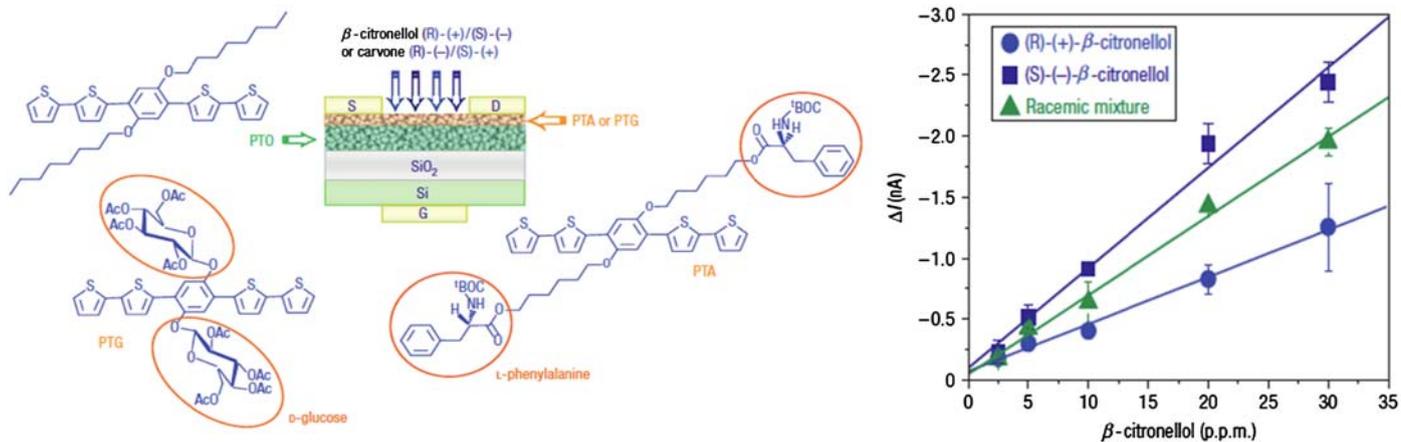


FIGURE 8 (Left) Structure of a bilayer organic field-effect transistor chiral sensor. (Right) Calibration curves of the chiral bilayer organic thin-film transistors exposed to (S)-(-)- β -citronellol, (R)-(+)- β -citronellol and to the racemic mixture. Adapted from L. Torsi, G.M. Farinola, F. Marinelli, M.C. Tanese, O.H. Omar, L. Valli, et al. *Nat. Mater.* 7 (2008) 412–417. Copyrights Nature Publishing Group. Reproduced with permission.

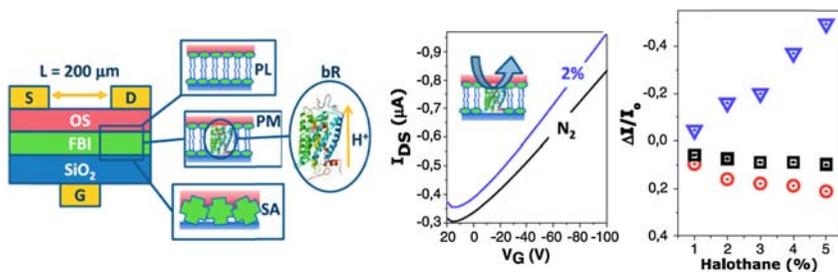


FIGURE 9 (Left) Structure of an FBI-OFET bearing a phospholipid bilayer (PL), purple membrane (dark grey in print versions) (PM) and streptavidin (SA). (Centre) FBI-PM OFET response to 2% halothane vapours and (Right) calibration curve for the FBI-PM OFET when exposed to different concentrations of halothane. FBI, Functional BioInterlayer; OFET, organic field-effect transistor. Adapted from M.D. Angione, S. Cotrone, M. Magliulo, A. Mallardi, D. Altamura, C. Giannini, et al. *Proc. Natl. Acad. Sci.* 109 (2012) 6429–6434. Reproduced with permission.

(Functional BioInterlayer, Fig. 9) [70]. As a proof-of-principle the OFET was interfaced with a purple membrane bio-receptor, and its selective response to an anaesthetic, halothane vapours, was investigated and reported.

The sensing mechanism behind OFET gas sensors can be pictured as a disruption at the semiconductor/dielectric interface when the semiconductor is exposed to the gas analyte. This will cause changes in the FET electrical performance due to trapping/detrapping of charges and increase/decrease of potential barrier between grains. The gas molecules can be absorbed on, be trapped between grain boundaries or even permeate the semiconductor layer.

A comparative study [71] of gas sensing behaviour (Figs 10 and 11) for P3HT- and PBTTT-based OFETs was published in 2014. The authors

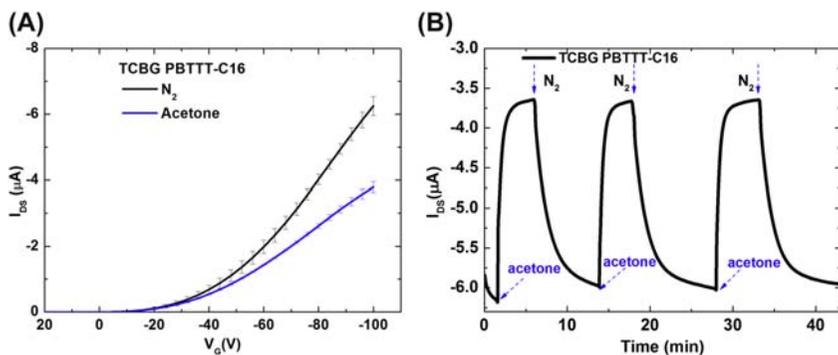


FIGURE 10 (A) Transfer characteristics recorded under nitrogen and after the top-contacts bottom-gate (TCBG) PBTTT-C16 sensor was exposed to acetone. (B) Transient drain current (I_{DS}) measurements when the sensor is exposed three times to acetone vapours (as = 0.5 at -6.6°C). From K. Manoli, L.M. Dumitru, M.Y. Mulla, M. Magliulo, C. Di Franco, M.V. Santacroce, et al. *Sensors (Basel)* 14 (2014) 16869–16880. Reproduced with permission.

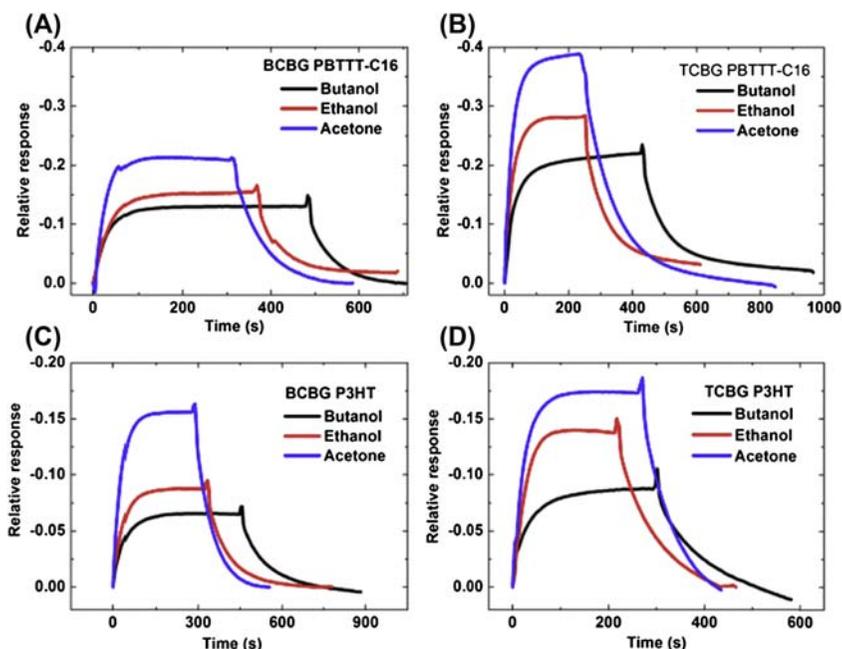


FIGURE 11 Transient drain current (I_{DS}) measurements of the OTFT-based sensors exposed to the three analytes at the same activity (as = 0.5 at -6.6°C). (A) Top-contacts bottom-gate (TCBG) PBTTC-16. (B) Bottom-contacts bottom-gate (BCBG) PBTTC-16. (C) TCBG P3HT. (D) BCBG P3HT. From K. Manoli, L.M. Dumitru, M.Y. Mulla, M. Magliulo, C. Di Franco, M.V. Santacroce, et al. *Sensors (Basel)*. 14 (2014) 16869–16880. Reproduced with permission.

investigated the response of two OFET sensor architectures [top-contacts bottom-gate (TCBG) and bottom-contacts bottom-gate (BCBG)] when exposed to butanol, ethanol and acetone. A decrease of the drain current was observed for all sensors when exposed to polar analytes.

The results showed a higher drop in the current with the increase of the dipole moment for each analyte. Also the morphological structure of the two OSCs used in this study contributed to the different sensing response of the devices when exposed to the same analyte, as reported in Fig. 11.

The PBTTC-based sensors exhibited higher responses for the same analyte as compared to the P3HT-based sensors. Remarkably an increased sensitivity in the response for the TCBG sensor configuration was observed, as compared to the BCBG sensor. The authors ascribe this to bulk conductivity and a possible adsorption of analyte vapours on the gold electrodes.

Like in the example discussed above, analyte nature (dipole moment, electron affinity and molecular size) and the morphology of the semiconductor layer can play a crucial role in the sensor's response. By introducing functional groups to the side chain of the semiconductor, an increase in sensitivity can be

achieved [72]. It is very difficult to achieve a reasonably good gas sensing discrimination, especially when it comes to complex gas samples. This inconvenience can be somehow overcome by using bilayers in which one of the semiconductors is more sensitive to the analyte than to another one, or by using sensor arrays.

In some cases, the analyte can produce a positive or negative shift in the threshold voltage V_T . This behaviour was observed when OFET sensors were used to detect ammonia or nitrogen oxides. The threshold voltage can be very sensitive to any extra charge induced to or 'taken' from the system. Oxidant gas molecule can dope p-type OSCs, shifting the threshold to more positive values and increasing the drain-source current. Reducing agents (eg, NH_3) cause an opposite response, shifting the threshold to more negative values, and a decrease in the drain-source current can be observed.

All these examples demonstrated that these OFETs are excellent multi-parameter gas-sensing platforms, reaching limits of detection in the range of parts-per-million due to signal amplification. These devices are cheap, give a fast response and are compatible with mass production techniques and can be easily integrated into smart packaging. However, even though remarkable new materials are being synthesized every day, selectivity of these devices remains an open issue.

OFET-based sensors can be produced also by interfacing the OSC with pure water [73], an electrolyte solution [74] or a solid electrolyte layer [75]. [76] In this case the devices are referred to as EGOFETs and are suitable candidates for liquid-sensing applications [77]. Sub-volt operation is possible due to the high capacitance of the two electric double layers formed when operating the device. Such a device is depicted in Fig. 12, along with the schematic representation of the operating mechanism.

The gating is achieved through the formation of EDL or Debye-Helmholtz layer at the gate–electrolyte and electrolyte–OSC interfaces. Both of these two interfaces can be used to integrate bio-receptors. Biscarini's group was one of the pioneers to prove that by functionalizing the top gold electrode of an EGOFET with boronic acid, picomolar concentrations of dopamine can be detected in a phosphate buffer solution [78].

A remarkably sensitive EGOFET, showed in Fig. 13, able to differentiate odorant chiral molecules was proposed by Mulla et al. in 2015. A mutant odorant-binding protein (OBP) was immobilized on the top gold electrode by means of a self-assembled monolayer (SAM) technique [79].

The OBP-functionalized EGOFET was able to detect and discriminate (S)- and (R)-carvone enantiomers down to picomolar concentration. A limit of detection of 50 pM was estimated for this detection method, which is almost six order of magnitude better than the limit reported in previous studies where carvone was detected using FET-based sensors [69] (Fig. 14).

Also the OSC–electrolyte interface can be used for sensing applications. Biotin can be immobilized on a phospholipid bilayer (PL), anchored on a

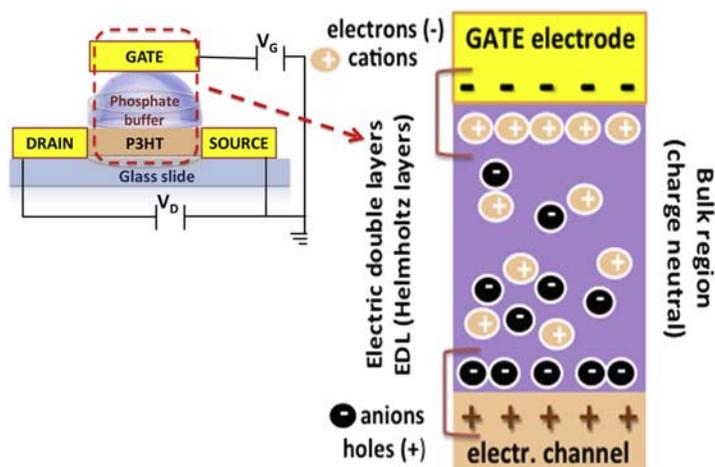


FIGURE 12 (Left) Schematic cross-section of an electrolyte-gated organic field-effect transistor gated with a droplet of phosphate buffer. (Right) Operation mechanism and formation of electric double layer at the two interfaces, when the gate is polarized. *Adapted from S.H. Kim, K. Hong, W. Xie, K.H. Lee, S. Zhang, T.P. Lodge, et al. Adv. Mater. 25 (2013) 1822–1846. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.*

P3HT layer. The PL is used both for immobilization of biotin, but it can also act as a barrier preventing chemical doping of the OSC [74]. This phenomenon can sometimes occur during EGOFET operation as small free ions, present in the electrolyte, might penetrate into the semiconductor's bulk and dope it. The proposed sensor was afterwards used for streptavidin detection and an increase in the drain-source current could be observed. It is speculated that this increase

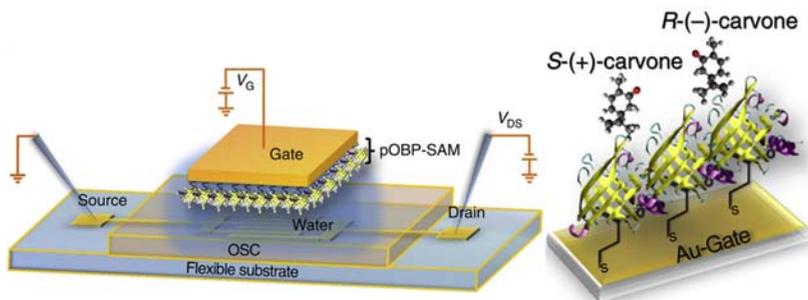


FIGURE 13 (Left) Schematic representation of a water-gated organic field-effect transistor for chiral discrimination. (Right) Top gold electrode functionalized with the odorant-binding protein (OBP). OSC, Organic semiconductor; SAM, self-assembled monolayer. *Adapted from M.Y. Mulla, E. Tuccori, M. Magliulo, G. Lattanzi, G. Palazzo, K. Persaud, et al. Nat. Commun. 6 (2015) 6010. Copyrights Macmillan Publishers Limited – Nature Communications. Reproduced with permission.*

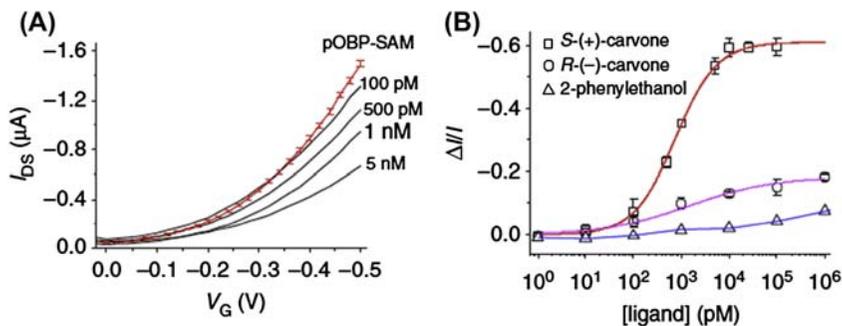


FIGURE 14 (A) Transfer characteristics are for a pristine pOBP-SAM gate (*red curve* (light grey in print versions)) and for a gate exposed to concentrations of (S)-(β)-carvone in the 100 pM–5 nM range (*black*). (B) Transfer characteristics normalized source-drain current changes ($\Delta I/I_0$) when the devices were exposed to the (R)-(β)- and (S)-(β)-carvone well as the 2-phenylethanol ligands. SAM, Self-assembled monolayer; OBP, odorant-binding protein. Adapted from M.Y. Mulla, E. Tuccori, M. Magliulo, G. Lattanzi, G. Palazzo, K. Persaud, et al. *Nat. Commun.* 6 (2015) 6010. Copyrights Macmillan Publishers Limited – Nature Communications. Reproduced with permission.

in current is due to the extra negatively charges brought by the streptavidin (negatively charged at that pH), after binding to biotin.

Other strategies for EGOFET biosensors include the use of cross-linked alginic acid capsules (Fig. 15) as ion-permeable polymeric gating electrolyte [80]. This versatile, biodegradable and biocompatible polymer was used both as electrolyte medium and as matrix for incorporating bio-receptors.

The strategy of using such a material is truly revolutionary, and this polymeric membrane can not only prevent liquid from evaporating during device operation but also serve as reactor for bio-enzymatic reactions. To prove this, the authors immobilized streptavidin inside the capsule, and the capsule was afterwards incubated with a solution containing fluorescence-labelled biotin. By means of fluorescent microscopy, the streptavidin–biotin

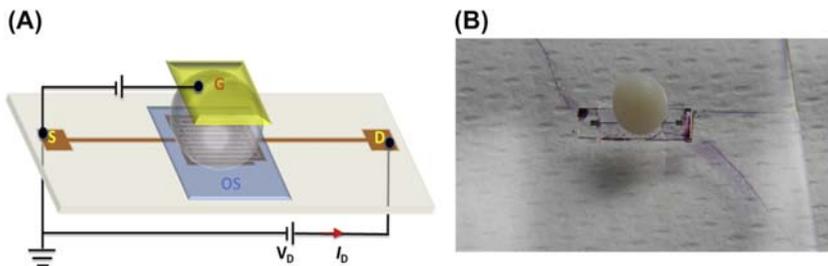


FIGURE 15 (A) Schematic representation of an electrolyte-gated organic field-effect transistor gated using an alginic acid capsule illustration. (B) Picture of an actual device bearing the alginic acid capsule. From L.M. Dumitru, K. Manoli, M. Magliulo, T. Ligonzo, G. Palazzo, L. Torsi, *APL Mater.* 3 (2015) 014904. Copyright AIP Publishing. Reproduced with permission.

binding could be observed. Also the well-known colorimetric assay for glucose detection was reproduced inside the alginate capsules. For this purpose, glucose oxidase (GOx) and horseradish peroxidase (HRP) were previously mixed with the biopolymer. When the prepared capsules were immersed in different concentration of glucose, a specific blue-green colour could be observed, as showed in Fig. 16.

In a proof-of-principle, the authors demonstrated that an EGOFET could monitor the reactions taking place inside the capsules. Even though this glucose biosensor is far from being a state-of-the-art glucose sensor, these preliminary results are extremely promising for low-cost, low-power, flexible bio-analytical applications for food industry.

4.5 Conclusions

The purpose of this chapter was to highlight the recent advances in the field of bio-organic electronics concerning analytical applications for the food industry. Nature is a massive reservoir of inspiration and offers endless possibilities in terms of biodegradable, biofunctional and biocompatible materials that can be used for the fabrication of smart sensing devices. So far many naturally occurring small molecules and polymers were demonstrated to function with good performance in organic electronic devices. Examples comprise DNA and nucleobases [9,10,55,81–83], various sugars [10], the biopolymer shellac [84,85], indigo and tyrian purple [84,86], cellulose [87,88], silk [89–91], waxes [92], protein, peptides and aminoacids [93,94] as well as biodegradable polymers in various forms [95,96]. Although such materials have been so far only part of small-scale laboratory demonstrations, the fact that silk, for example, could be used as robust platform for fabrication of high

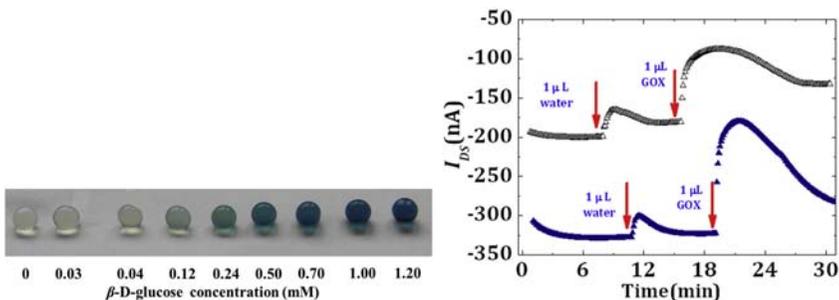


FIGURE 16 (Left) Alginate GOx/HRP-based capsules colorimetric assay for different glucose concentrations. (Right) Transient electronic detection of an enzymatic assay using an alginate capsule gating the EGOFET sensor. HRP, Horseradish peroxidase; GOx, glucose oxidase; EGOFET, electrolyte-gated organic field-effect transistor. Adapted from L.M. Dumitru, K. Manoli, M. Magliulo, T. Ligonzo, G. Palazzo, L. Torsi, *APL Mater.* 3 (2015) 014904. Copyright AIP Publishing. Reproduced with permission.

performance, transient, integrated electronics [97] demonstrates the immense versatility of natural materials that can be tailored to virtually any specific application involving biocompatibility. There is still a long way till such devices will become reliable and cheap enough to replace the traditional analytical techniques; however, we can only imagine the possibilities.

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