

# Material Matters™

VOLUME 18 • NUMBER 1

## Greener Electronics

Conducting Bio-based Polymers and Composites for Advanced Applications

Towards Greener Organic Transistor Sensors

Nature as the Source of Materials More Sustainable Organic Electronics

Substrate and Conductor Materials Towards More Sustainable Electronics

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## Introduction



**Monica Jung de Andrade, Ph.D.**  
Global Product Manager  
– Electronic Materials  
Materials Science

Welcome to issue 18.1 of *Material Matters*™, Greener Electronics. This issue highlights current trends associated with more sustainable materials used in advanced electronic applications. Conductive bio-based polymers and composites are critical in making greener sensors and organic electronics.

In our first article, **Professor Ernesto C. Pereira and colleagues (Campinas State University, Federal University of São Carlos)** review recent advances in conducting bio-based polymers and composites for flexible and bioelectronics, and such as (bio-)sensors, supercapacitors, active drug delivery, and nerve probes. They outline the significant “green” potential in a world focused on sustainability, such as graphene produced from biomass. And the importance of well-established testing methods on biodegradability to regulate the durability properties of these materials in various simulated weather conditions.

In our second article, **Professor Soniya D. Yambem and Ph.D. student Joshua N. Arthur (Queensland University of Technology)** examine advances in greener materials used in electrodes, substrates, insulators, and electrolytes for organic transistors (OTFTs, OFETs, OECTs and EGOFTs), with a special focus on Organic Thin Film Transistors (OTFTs). They highlight several advances in the various components of OTFT (Organic Thin Film Transistors) sensors and that a careful choice of materials is urged to integrate the many existing insights into entirely eco-friendly OTFT sensors.

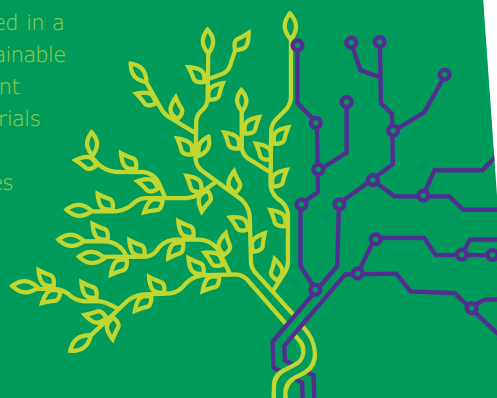
**Professor Clara Santato and team (Polytechnique Montréal)** describe how sustainable organic electronics (SOE) are transforming the electronics field from dramatic accumulation of e-waste and depletion of certain (critical or endangered) chemical elements towards the next generation of organic electronics, in our third article. Here, Santanato et al. discuss the challenges and opportunities within organic electronic materials selection, emphasizing their use towards energy conversion and storage. Further, they outline the importance of additive manufacturing printing technologies to reduce waste, energy, and the overall cost of device fabrication with the added benefit of flexible, lightweight devices.

In our final article, **Professor Maria Smolander and colleagues (VTT Technical Research Center in Finland)** report the latest advances in sustainable substrates and conductive materials for flexible electronics. The team highlights advances in organic photovoltaic (OPV), supercapacitor, and NFC communication. They highlight the growing potential of bioelectronics and the exploitation of the intrinsic properties of sustainable materials towards ‘greener’ electronics. Lastly, they stress the importance of considering a comprehensive approach for device manufacturing, such as solvent-based inks containing Volatile Organic Compounds (VOCs), and life cycle assessments, such as how energy-intensive they are to produce and recycle.

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# Table of Contents

## Articles

|  |    |
|--|----|
| Conducting Bio-based Polymers and Composites for Advanced Applications     | 3  |
| Towards Greener Organic Transistor Sensors                                 | 11 |
| Nature as the Source of Materials for More Sustainable Organic Electronics | 18 |
| Substrate and Conductor Materials Towards More Sustainable Electronics     | 24 |

## Featured Products

Products with this icon  displayed are identified as greener alternative products.

|   |    |
|---|----|
| Bio-based Polymers<br>A selection of bio-based polymers for advanced applications   | 8  |
| Conducting Polymers<br>A selection of PEDOT:PSS, polyaniline, and polypyrrole conducting polymers   | 9  |
| 2D Nanomaterial Fillers<br>A selection of MXene precursors and graphene-based products  | 10 |
| Organic Semiconductors<br>A selection of organic hole transport and organic electron transport materials (n-type)                         | 15 |
| Biosourced Solvents<br>A list of biosourced solvents for electronic Applications  | 21 |
| Semiconducting Materials<br>A selection of singlewalled carbon nanotubes and inorganic inks   | 22 |
| Carbon Nanomaterials and Conductive Inks<br>A selection of conductive carbon nanotubes and conductive inks                                | 27 |
| Flexible Substrates<br>A selection of biodegradable substrates, recyclable flexible substrates, and conductive coated flexible substrates | 28 |

## Your Material Matters



Nicolynn Davis, Ph.D.  
Head of Material Sciences and F&F

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| 3D Printable Ultra-High Temperature Boron Carbide Ink    | 921912   |
| 3D Printable Yttria-stabilized Zirconium (IV) Oxide Ink  | 918571   |

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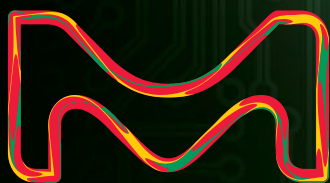
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# Conducting Bio-based Polymers and Composites for Advanced Applications



Roger Gonçalves,<sup>1,3</sup> Marco A. B. Ferreira,<sup>1</sup> Ernesto C. Pereira<sup>1,2,3\*</sup>

<sup>1</sup> Center for Innovation on New Energies, Institute of Chemistry, Campinas State University, Campinas – SP, Brazil

<sup>2</sup> Center of Excellence for Research in Sustainable Chemistry, Department of Chemistry, Federal University of São Carlos, São Carlos – SP, Brazil

<sup>3</sup> Center for Research and Development of Functional Materials, Department of Chemistry, Federal University of São Carlos, São Carlos – SP, Brazil

\*Email: ernesto@ufscar.br

## Introduction

Climate change has become a harsh reality that cannot be ignored. To hinder its destructive impact, it is imperative to move towards a clean energy matrix with low dependence on fossil fuels and decrease the number of residues dispersed in the environment. Bio-based polymers can be essential in reducing electrical and electronic waste and increasing service life for targeted applications. This mini-review discusses the recent achievements in bio-based polymer synthesis, their properties, and their applications as composites.

Requiring renewable and greener pathways, the accelerating need for energy combined with the current call for sustainable growth is one of the most critical challenges in contemporary societies. Biomass is becoming a viable alternative or complementary source for obtaining petroleum-derived products, such as fuels, polymers, and fine chemicals. In this minireview, we discuss the recent achievements in conductive bio-based polymers and their applications in bioelectronics, sensors, and supercapacitors.

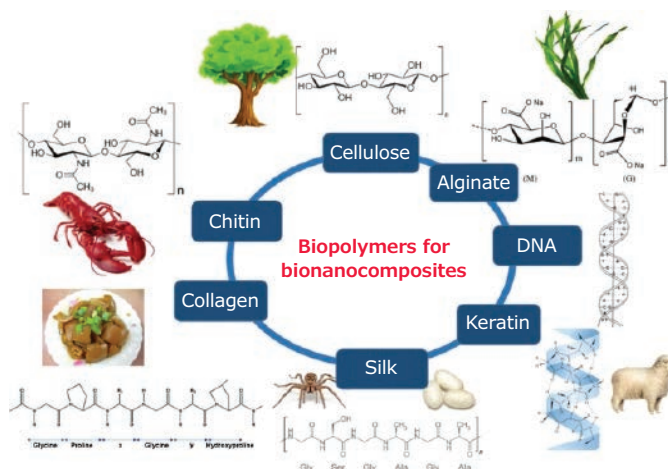
## Functional Materials for Greener Composites

The synthesis of sustainable materials for renewable energy generation has been the focus of substantial research in recent years.<sup>1</sup> The fundamental challenges are long cycle life, high functionality, high performance, low cost, and biodegradability.

Materials such as carbon composites, hybrid materials, and engineered polymers can be optimized to satisfy these five criteria. Among these emerging resources, pure and composite bio-based polymers are promising to build cleaner and sustainable energy devices. In addition, the appeal for greener technological solutions encourages scientists to seek inspiration in nature itself, stimulating a new genre of research focused on the development of bio-inspired materials.<sup>2</sup>

## Bio-based Polymers

Biopolymers, illustrated in **Figure 1**, are produced by living beings or obtained from renewable sources of raw materials, making them a greener alternative to conventional polymers. One great advantage of using biopolymers is their biodegradability in the environment. The degradation of these macromolecules results from the action of naturally occurring microorganisms.<sup>1,2</sup> Therefore, biopolymers are gaining traction due to these characteristics increasing their useful life cycle and disposability. “Greener polymers”, such as “green” polyethylene (PE), are also widely employed. Greener PE has the same applications as fossil-based PE, with the extra advantage of capturing CO<sub>2</sub> from the atmosphere during its production.<sup>3</sup>



**Figure 1.** Example of biopolymers sourced from either animal or plant. Reprinted with permission from reference 3, copyright 2018, Elsevier.

Biopolymers have also been investigated to replace the conventional active metals and alloys used in smart devices for increased energy saving.<sup>3</sup> Active materials respond to external stimuli such as pH, temperature, humidity, and electricity by changing its shape, color, and/or size. This technological application trend occurs due to the intrinsic properties of polymers, such as low density, low cost, fracture resistance, malleability, easy processability, and fabrication.<sup>4</sup>

While several active polymers respond to electrical stimuli,<sup>1</sup> biopolymers are nonelectrical conductor materials. Thus, electrically conductive fillers dispersed in the biopolymer matrix have been investigated.<sup>5</sup> The filler dispersion in the matrix determines the percolation pathway for an electrically conductivity composite. Discussed next are the different dispersion techniques used to prepare conductive composites.

### Preparation of Bio-based Composites

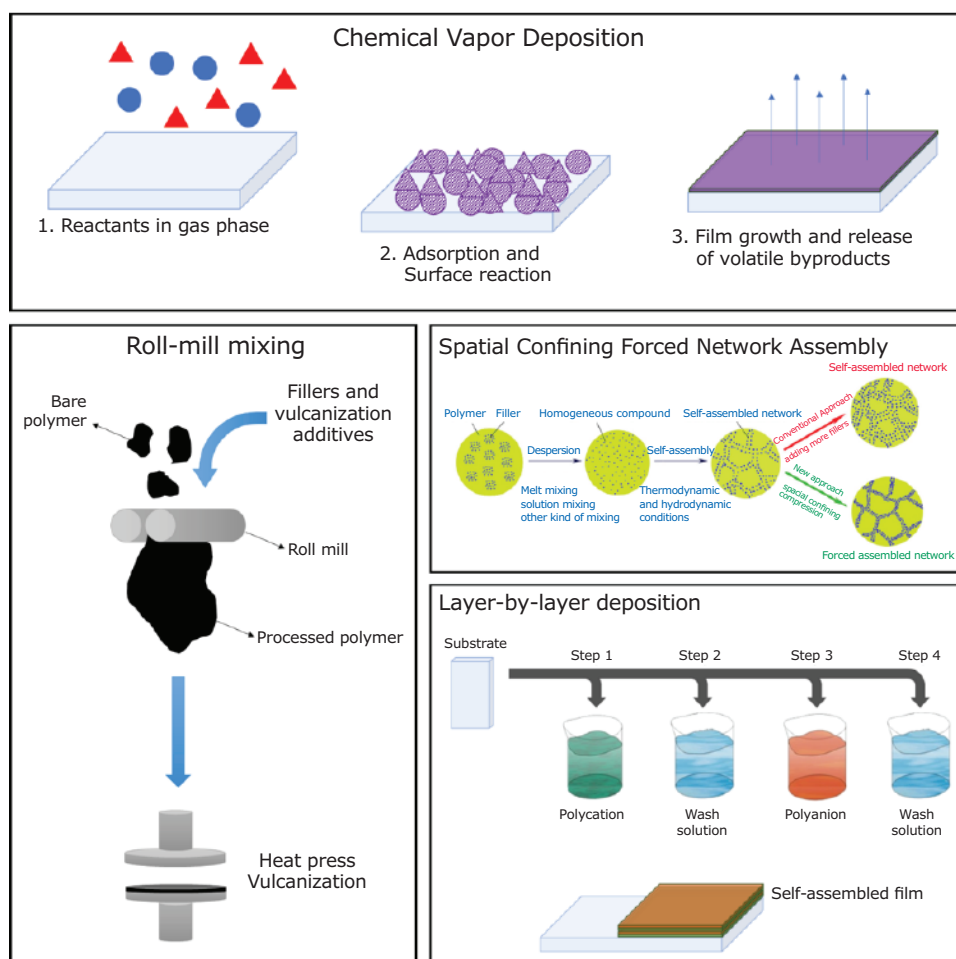
Purely physical mixing techniques such as high-speed mixing, melting mixing, and roll milling are conventional procedures to synthesize polymer composites. Each of these methods relies on shear forces to cause a filler to disperse in a polymer matrix. However, under different conditions, these processes could produce a lower-quality material. These techniques do not permit

the addition of compatibilizers that improve dispersion, requiring the fillers to be pre-emptively modified.

Another approach is the use of chemical processes to improve dispersion. Among them are such techniques as chemical vapor deposition and *in situ* polymerization. While these processes are efficient, they require additional steps and have an increased cost for industrial scale-up. However, they also allow for the addition of compatibilizers without the need to modify both matrix and/or fillers.

One innovative approach is the Spatial Confining Forced Network Assembly (SCFNA) technique which allows for great conductivity using minimum filler. The electrical conductivity of short polypropylene/carbon fibers prepared using this method is up to four orders of magnitude above those produced using common incorporation technology.<sup>2</sup> Also worthy of mention is a self-assembling technique involving the use of a poly-cation and a poly-anion in which electrostatic interaction enables the formation of a film. The low-cost point of this procedure and the possibility of preparing polycation/polyanion films comprised of upwards of a hundred layers make it an attractive method.<sup>6</sup>

Figure 2 schematically represents the several types of methods used to disperse conductive charges in polymer matrices.



**Figure 2.** Illustrative scheme of different techniques of dispersion of conductive fillers in polymeric matrices. Partially reprinted under Creative Commons Attribution License.



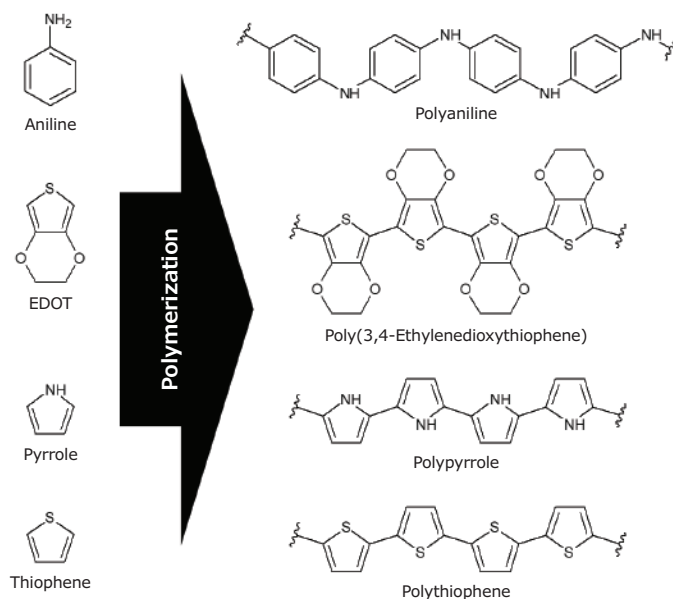
## High-performance Bio-based Composites

Plant and bacteria celluloses are excellent examples of easily produced biopolymers from renewable sources. The following subsection will present the most recent advances in biopolymer applications.

Farjana et al.<sup>7</sup> obtained a flexible sensor from bacterial cellulose and a solution containing 1 mg of carbon nanotubes (CNT) (Cat. Nos. **901019**, **900788**, **755168**) per mL of cellulose. The conductive composite (up to 1.6 mS cm<sup>-1</sup>), showed excellent mechanical properties and a good electrical response to deformation. In a different publication, Sen et al.<sup>8</sup> used cellulose and graphene (Cat. No. **900561**) nanocomposite to obtain a composite with electrical conductivity of 5.1 mS/cm using only 0.50 wt.% graphene filler. Using another approach, Peng et al.<sup>9</sup> fabricated graphene-cellulose nanocomposite films by casting using imidazolium-based ionic liquids (Cat. No. **900771**). These films showed conductivities of up to 10 mS/cm starting from 200 mL of a solution containing 80 mg of rGO and 30 g of [BMIM]Cl. Also using ionic liquids, Javed et al.<sup>10</sup> obtained nanofibers by electrospinning based on cellulose acetate (Cat. Nos. **419028**, **180955**), graphene oxide (GO, Cat. No. **921556**) and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl, Cat. No. **94128**). The combined advantages of GO and [BMIM]Cl materials allow for the homogeneous dispersion of GO and better solubility of cellulose, demonstrating the compatibility effect these ionic liquids confer on polymeric matrices.<sup>11</sup> A concentration of only 0.43 wt.% of graphene oxide was enough to give a conductivity of 5.30 mS/cm.

As previously stated, the electrical conductivity of biopolymers is extremely low, while synthetic polymers, such as polyaniline (PAni, Cat. No. **912891**), poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrole (PPy, Cat. No. **912573**), and polythiophene (PTh) have high electrical conductivity (Figure 3). While these polymers show good biocompatibility, their low degradability is a critical detractor for their use. A strategy to improve this proclivity is combining the synthetic with biopolymers, obtaining conductive compounds with strong biodegradability and excellent biocompatibility. The challenge in synthesizing these composites is finding the best composition to maximize electrical conductivity and minimize the proportion of non-degradable conjugate components. Another approach, in line with the precept of bioinspiration, is the use of conventional molecules, such as carotene derivatives (Figure 5A), present in carrots, to produce conductive composites based on a single molecule.<sup>12</sup> Although the performance is not yet comparable to that of conductive macromolecules, it is a very promising field of research.

PAni has attracted significant attention due to its high electrical conductivity, easy synthesis in aqueous media, excellent thermal and environmental stability, controllable electrical conductivity, and ease of structural modification. This polymer has promising future applications in flexible electronics, such as electrodes and strain sensors.<sup>13</sup> To use a biodegradable matrix and take advantage of the conductive properties of polyaniline, Han et al.,<sup>14</sup>

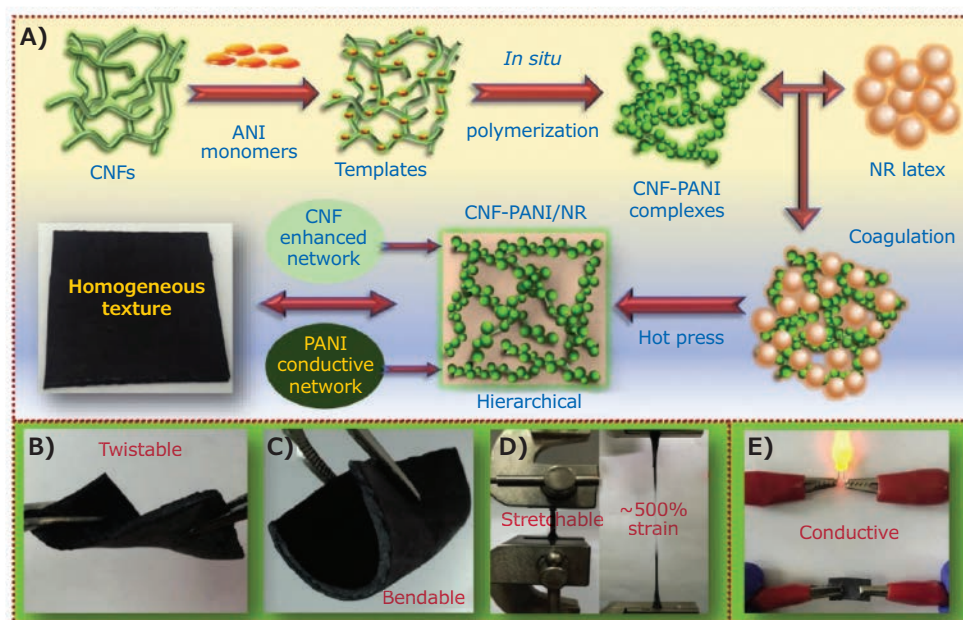


**Figure 3.** Chemical structure of the main monomers and their respective conducting polymers.

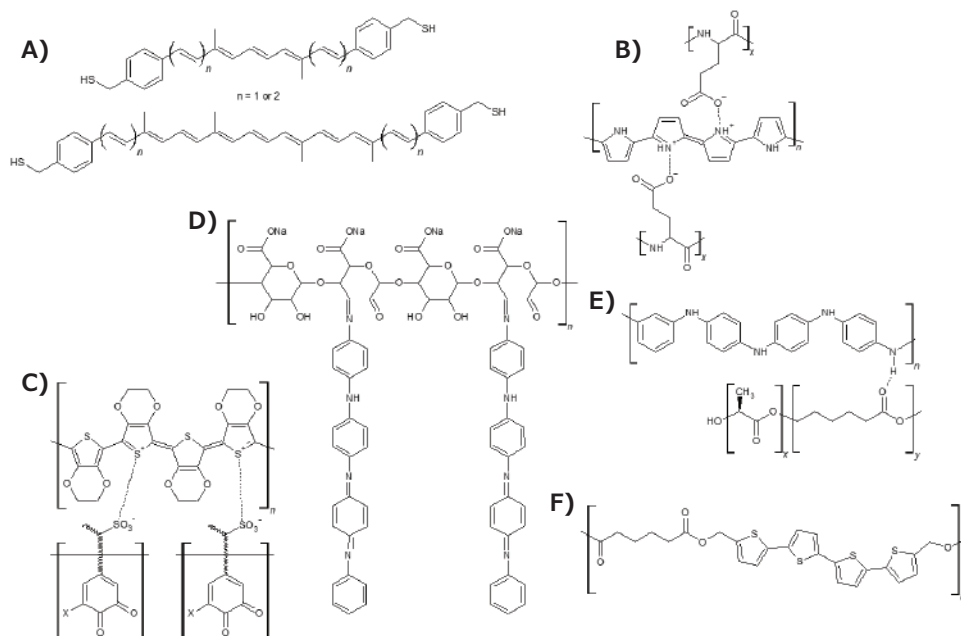
studied the *in situ* polymerization of aniline in a nano cellulose (Cat. No. **561126**) template to incorporate it into a natural rubber matrix (Figure 4). Aniline was integrated into the rubber via cellulose nanofiber (CNF) polymerization and complexation ensuring a better dispersion of the conductive portion and resulting in a homogeneous and flexible conductive composite (up to 90 mS m<sup>-1</sup>). The material was characterized as a strain sensor and supercapacitor, demonstrating excellent performance for both applications.

PPy was among the first conductive polymers studied and has been widely used in bioelectronics and biosensors. It is prepared by the electrochemical or chemical oxidation of pyrrole. Different dopants can be inserted during its oxidation, affecting its conductive properties. An example of this phenomenon is how the introduction of poly(L-glutamic acid) as a dopant in PPy (Figure 5B) provides acid groups that further improve PPy's electrical conductivity and biodegradability.<sup>15</sup> Additionally, polypyrrole-*block*-poly(caprolactone) (Cat. No. **735817**) is another biodegradable conducting polymer.

PEDOT is a conductive polymer based on the monomer 3,4-ethylenedioxythiophene (EDOT). PEDOT nanotubes have been successfully used for neural recording, closely mimicking the abilities of neurons.<sup>16</sup> Additionally, the poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS, Cat. No. **900208**) composite is in regular use due to its unique properties, such as excellent conductivity, good stability, high optical transparency, and low toxicity. Therefore, due to the need for the presence of a second chain to improve the properties of PEDOT, using lignin (Cat. No. **370959**) as a biopolymer



**Figure 4.** A) Schematic illustration for the preparation and synthesis process of conductive CNF-PANI/NR hybrid elastomers with a hierarchical 3D network structure and the demonstration of their B) flexibility, C) bendability, D) stretchability, and E) conductivity. Reprinted with permission from reference 14, copyright 2019 Elsevier.



**Figure 5.** Chemical structure of bio-composites based on conductive polymers: A) carotene analogues, B) Ppy doped with poly(L-glutamic acid), C) PEDOT:lignin, D) oligo PANi-graphitized polysaccharide, E) polyaniline/poly[(L-lactide)-co-(ε-caprolactone)], and F) 5''-bis(hydroxymethyl)-3,3''-dimethyl-2,2':5',2'':5'',2''-quaterthiophene-co-adipic acid polyester.

(Figure 5C) has also conferred greater biodegradability to the composites of this conductive polymer without any damage to its conductive property, as lignin also acts as a dopant molecule and is successfully used as supercapacitor material.<sup>17</sup>

To improve poor mechanical properties, hydrophobicity, and non-degradability of these intrinsically conductive polymers, blends with biopolymers have been explored and extensively researched.<sup>1</sup> Some successful biopolymers for these mixtures

include polylactide (PLA, Cat. Nos. **764620**, **764612**, **767344**), polycaprolactone (PCL, Cat. Nos. **440744**, **440752**), poly(lactide-co-glycolide) (PLGA, Cat. Nos. **901021**, **790214**, **900316**, **900289**), polycaprolactone fumarate, poly(lactide-co-polycaprolactone) (PLA-co-PCL, Cat. Nos. **900321**, **900300**, **900312**), polyurethane (Cat. No. **446084**), chitosan (Cat. Nos. **C3646**), gelatin (Cat. No. **1.04078**), collagen (Cat. No. **234149**), and heparin (Cat. No. **Y0001282**). It is important to mention that the application of biopolymers to produce biodegradable



composites has been subject to well-established testing methods, such as ISO 14855-2, which regulates the durability properties of these materials in various simulated weather conditions.<sup>18</sup>

Wang et al.<sup>19</sup> produced a polymer based on a polysaccharide backbone graphitized with polyaniline tetramers (**Figure 5D**) that is water soluble, biodegradable, electroactive, and noncytotoxic. Additionally, this innovative polymer exhibited electroactivity, reversible redox capabilities, and reversible doping/de-doping properties, proving to be an excellent candidate for medical applications, such as biosensors, active drug delivery, and nerve probes. Thus, regarding biomedical application, a polyaniline (**Cat. No. 912891**) enhanced poly[(L-lactide)-co-(ε-caprolactone)] copolymer (**Cat. No. 769851**) developed by Bhang et al.<sup>20</sup> (**Figure 5E**) was used for the control of neural cell function. The fibers of this polymer were synthesized by electrospinning and then placed in PC12 cell culture medium, obtaining a porous material with a regular structure and with great neuro-regenerative capacity. To guarantee biodegradability and obtain electrical conductivity, Guimard and collaborators<sup>21</sup> studied the incorporation of thiophene oligomers (**Cat. No. T31801**) in natural polyester, obtaining a conductive bio co-polymer. By means of a simple polycondensation reaction, alternating electroactive quaterthiophene units and biodegradable ester units were copolymerized resulting in the novel polymer 5,5'''-bis(hydroxymethyl)-3,3'''-dimethyl-2,2':5',2'':5'',2''-quaterthiophene-co-adipic acid polyester (QAPE) (**Figure 5F**). This material exhibited redox activity via cyclic voltammetry as well as red-shifted absorption peaks upon doping, confirming that the quaterthiophene units maintain their electroactivity. These examples demonstrate how wide and promising the use of

bio-based composites for different applications can be, especially in greener and clean energy processes and devices.

**Table 1** summarizes the essential bio-based composites covered in the review along with their primary application and electrical conductivity magnitude, the most critical property for this type of material.

## Final Considerations and Future Challenges

Although the development of conductive bio-based polymers still has a substantial way to go before replacing conventional polymer composites, they exhibit significant “green” potential in a world where sustainability is in focus. That said, critical improvements are still necessary for this vision to be realized. In particular, the fillers currently used to increase the conductivity of these composites are neither biodegradable nor “green”, and ongoing effort is still required to discover additives that match the low environmental impact of the base material. Fortunately, research investigating the production of more sustainable conductive loads has attracted considerable attention and important work has been done — much like in the case of graphene produced from biomass.<sup>22</sup> In these possibilities, there is great room for optimism.

## Acknowledgments

The authors acknowledge the financial support provided by GlaxoSmithKline, Brazilian National Council for Scientific and Technological Development — CNPq, São Paulo Research Foundation (grants no. 2013/07296-2, 2014/50249-8, 2017/11986-5), and the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES – Finance Code 001).

**Table 1.** Composition of some bio-based composites and their applications.





| Matrix                                | Filler                    | Conductivity (S cm <sup>-1</sup> ) | Application                    | Characteristic                                 | Ref. |
|---------------------------------------|---------------------------|------------------------------------|--------------------------------|--|------|
| Polypropylene                         | Short carbon fibers       | 1.032                              | Conductive substrate           | biodegradable and biocompatible                | 2    |
| Bacterial cellulose                   | carbon nanotubes          | up to 1.6                          | Sensor                         | biodegradable                                  | 7    |
| Cellulose                             | graphene                  | 5.1×10 <sup>-3</sup>               | Sensor                         | biodegradable                                  | 8    |
| Cellulose                             | graphene + [BMIM]Cl       | 10×10 <sup>-3</sup>                | Conductive substrate           | biodegradable                                  | 10   |
| Cellulose acetate                     | graphene oxide + [BMIM]Cl | 5.3×10 <sup>-3</sup>               | Conductive fibers              | biodegradable                                  | 11   |
| Natural rubber                        | nanocellulose + PANi      | 0.895                              | Strain sensor / supercapacitor | biodegradable and biocompatible                | 14   |
| poly (L-glutamic acid)                | Polypyrrole               | ~10                                | Bioelectronics                 | biodegradable and biocompatible                | 15   |
| Lignin                                | PEDOT                     | *                                  | Supercapacitor                 | biodegradable                                  | 17   |
| poly[(L-lactide)-co-(ε-caprolactone)] | PANi                      | -                                  | Neural cell controlling        | Biodegradable, biocompatible and non-cytotoxic | 20   |

\* Reported an increase of 110% when compared to pristine PEDOT.

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## Bio-based Polymers

| Name                            | Form  | Average Mn / Feed Ratio    | Viscosity / Density                  | Cat. No. |
|---------------------------------|---|----------------------------|--------------------------------------|----------|
| Bio-based Polyether Polyol      |  | 500                        | 90–120 mPa.s(40 °C)                  | 923990   |
|                                 |  | 1,000                      | 200–300 mPa.s(40 °C)                 | 923974   |
|                                 |  | 2,000                      | 750–900 mPa.s(40 °C)                 | 923966   |
|                                 |  | 2,700                      | 1550–1850 mPa.s(40 °C)               | 923982   |
| Poly(D,L-lactide)               | solid   | 5,000                      |                                      | 764612   |
|                                 | solid   | 10,000                     |                                      | 764620   |
|                                 | crystals  | 20,000 (NMR)               |                                      | 767344   |
| Poly(L-lactide-co-caprolactone) | chips or granules   | lactide:caprolactone 15:85 | 1.5 dL/g                             | 900312   |
|                                 | chips or granules   | lactide:caprolactone 35:65 | 1.5 dL/g                             | 900321   |
|                                 | chips or granules   | lactide:caprolactone 60:40 | 1.5 dL/g                             | 900300   |
| Poly(L-lactide-co-glycolide)    | chips   | lactide:glycolide 10:90±5  | 1.4–2.0 dL/g                         | 901021   |
|                                 | chips or granules   | lactide:glycolide 20:80    | 1.6 dL/g                             | 900289   |
|                                 | granular  | lactide:glycolide 5:95     | 1.1 dL/g (0.1% (w/v) in HFIP, 25 °C) | 790214   |
|                                 | granular  | lactide:glycolide 65:35    | 0.6 dL/g                             | 900316   |
| Polycaprolactone                | pellets (~3 mm)   | 80,000                     | 1.145 g/mL at 25 °C                  | 440744   |
|                                 | flakes or chunk(s)  | ~10,000 by GPC             | 400–1000 mPa.s, 50 wt. % in xylene   | 440752   |

## Conducting Polymers




### PEDOT:PSS

| Name  | Description  | Viscosity                                     | Cat. No. |
|---|--|---|----------|
| Graphene/PEDOT:PSS hybrid ink   | dispersion in DMF<br>0.2 mg/mL (PEDOT:PSS)<br>1 mg/mL (electrochemically exfoliated graphene)  |   | 900442   |
| Molybdenum trioxide/PEDOT:PSS ink   | 0.8 wt% crystalline MoO <sub>3</sub> /PEDOT:PSS  | 3 cP (25 °C) (6500s <sup>-1</sup> shear rate) | 901047   |
| Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)   |  0.8% in H <sub>2</sub> O, conductive inkjet ink                    | 7-12 cP(22 °C)                                | 739316   |
|   |  1.1% in H <sub>2</sub> O, neutral pH, high-conductivity grade      | <100 cP(22 °C)                                | 739324   |
|   |  1.1% in H <sub>2</sub> O, surfactant-free, high-conductivity grade | 30-100 cP(20 °C)                              | 739332   |
|   |  1.3 wt % dispersion in H <sub>2</sub> O, conductive grade          |   | 483095   |
|   | 2.8 wt % dispersion in H <sub>2</sub> O, low-conductivity grade  | <20 cP(20 °C)                                 | 560596   |
|   |  3.0-4.0% in H <sub>2</sub> O, high-conductivity grade              | 10-30 cP(20 °C)                               | 655201   |
|   |  5.0 wt. %, conductive screen printable ink                         | ≥50,000 mPa.s(20 °C)                          | 768650   |
|   | dry re-dispersible pellets   |   | 768618   |
|  dry re-dispersible pellets, high conductivity |  | 900208  |          |
|  high-conductivity grade                       |  | ≤70 mPa.s(20 °C)                              | 900181   |

### Polyaniline

| Name   | Average Mw | Description                               | Cat. No. |
|--|------------|---|----------|
| High surface area conducting polyaniline                     |            |   | 912891   |
| Polyaniline (emeraldine base)                                | ~5,000     | $\lambda_{\max}$ ~325 nm                  | 556459   |
|  | ~10,000    |   | 476706   |
|  | ~20,000    | $\lambda_{\max}$ 328 nm                   | 556378   |
|  | ~50,000    | $\lambda_{\max}$ 330 nm                   | 556386   |
|  | ~65,000    | $\lambda_{\max}$ 331 nm                   | 530689   |
|  | ~100,000   | $\lambda_{\max}$ ~324 nm                  | 576379   |
| Polyaniline (emeraldine salt)                                | >15,000    | conductivity: 2-4 S/cm (compacted powder) | 428329   |
| Polyaniline (emeraldine salt) short chain, grafted to lignin |            | conductivity: 1-2 S/cm (pressed pellet)   | 561126   |

### Polypyrrole




| Name  | Form  | Description | Conductivity  | Cat. No. |
|---|---|-------------|---|----------|
| High surface area conducting polypyrrole      |  black solid                                   |             |   | 912573   |
| Polypyrrole                                   |  5 wt % dispersion in H <sub>2</sub> O         | doped       | conductivity >0.005 S/cm (dried cast film)          | 482552   |
|   | ~5 wt. % loading, coated on titanium dioxide  | doped       | conductivity 0.5-1.5 S/cm (pressed pellet, typical) | 578177   |
|   |   | doped       | conductivity 10-50 S/cm (pressed pellet)            | 577030   |
|   |  20 wt. % loading, composite with carbon black | doped       | conductivity 30 S/cm (bulk)                         | 530573   |
|   | ~20 wt. % loading, composite with carbon black  | undoped     |   | 577065   |
| Polypyrrole- <i>block</i> -poly(caprolactone) | 0.3-0.7 wt. % dispersion in nitromethane  | doped       |   | 735817   |

## 2D Nanomaterial Fillers

### MXene Precursors

| Name   | Description                          | Particle Size          | Cat. No. |
|--|--------------------------------------|------------------------|----------|
| Molybdenum Titanium Aluminum Carbide MAX phase | $\text{Mo}_2\text{Ti}_2\text{AlC}_3$ |                        | 925977   |
| Niobium Aluminum Carbide MAX phase             | $\text{Nb}_2\text{AlC}$              |                        | 925195   |
|  | $\text{Nb}_4\text{AlC}_3$            |                        | 925985   |
| Titanium aluminium carbide 211                 | $\geq 80\%$                          | $\leq 40 \mu\text{m}$  | 910759   |
|  | $\geq 80\%$                          | $\leq 200 \mu\text{m}$ | 910708   |
|  | $\geq 80\%$                          | $\leq 100 \mu\text{m}$ | 910821   |
| Titanium aluminium carbide 312                 | $\geq 90\%$                          | $\leq 40 \mu\text{m}$  | 910775   |
|  | $\geq 90\%$                          | $\leq 100 \mu\text{m}$ | 910767   |
| Titanium Aluminum Carbonitride MAX phase       | $\text{Ti}_3\text{AlCN}$             |                        | 925950   |
| Titanium Aluminum Nitride MAX phase            | $\text{Ti}_2\text{AlN}$              |                        | 925969   |

### Graphene Based Materials

| Name   | Description   | Surface Area / Dimension  | Cat. No. |
|--|---|---|----------|
| Graphene                                       | powder, electrical conductivity $>10^3 \text{ S/m}$   | $>500 \text{ m}^2/\text{g}$ (BET)   | 900561   |
| Graphene nanoribbon                            | oxidatively splitted from CNT   | $\geq 200 \text{ nm}$ , Nanoribbon  | 922676   |
| Graphene nanoribbon                            | $\geq 90\%$ carbon basis (EA)   | $0.25\text{-}0.35 \mu\text{m}$  | 922714   |
| Single-layer graphene sheets for battery       |  Bio-sourced | $\leq 64 \mu\text{m}$ (ASTM Sieve analysis)<br>BET surf. area $1155.3 \text{ m}^2/\text{g}$           | 924458   |
| Nitrogen/Sulfur co-doped graphene oxide powder |  Bio-sourced | $25\text{-}30 \mu\text{m}$<br>BET surf. area $7.7 \text{ m}^2/\text{g}$ (method- Nitrogen adsorption) | 926817   |
| Nitrogen doped graphene oxide powder           |  Bio-sourced | $25\text{-}30 \mu\text{m}$<br>BET surf. area $2.4 \text{ m}^2/\text{g}$ (method- Nitrogen adsorption) | 926868   |

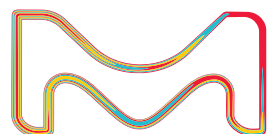
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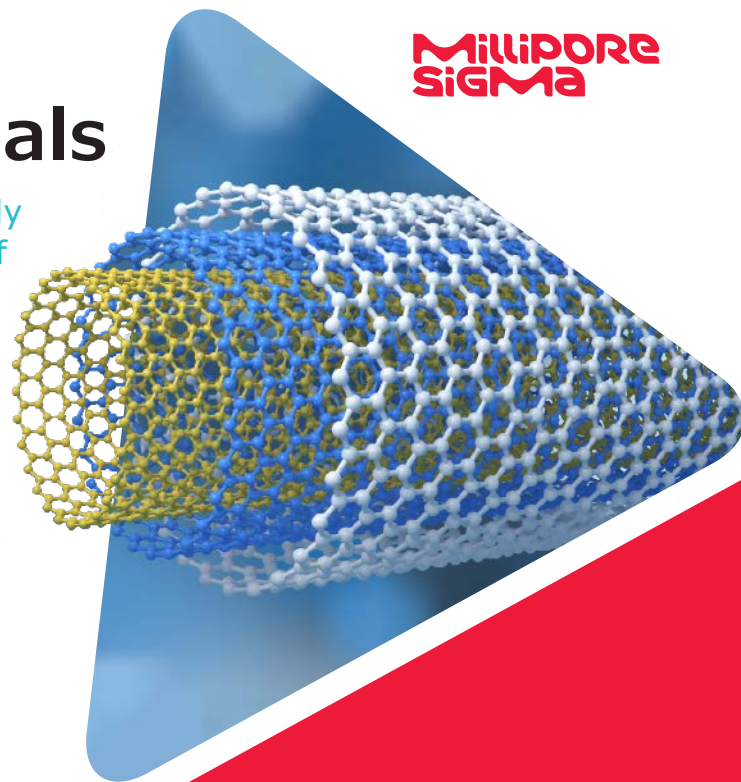
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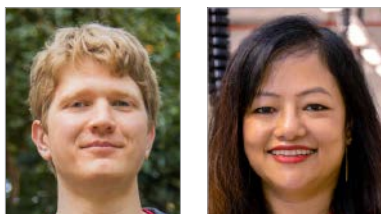
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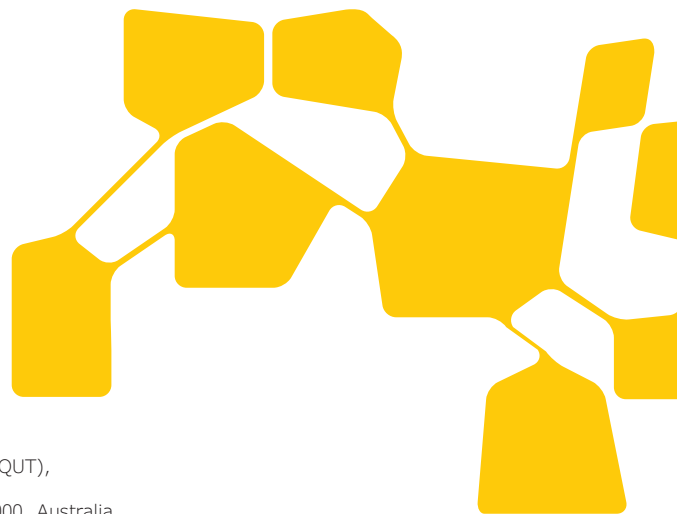


# Towards Greener Organic Transistor Sensors



Joshua N. Arthur & Soniya D. Yambem\*

School of Chemistry and Physics, Faculty of Science, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia  
Centre for Materials Science, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia  
\*Email: soniya.yambem@qut.edu.au

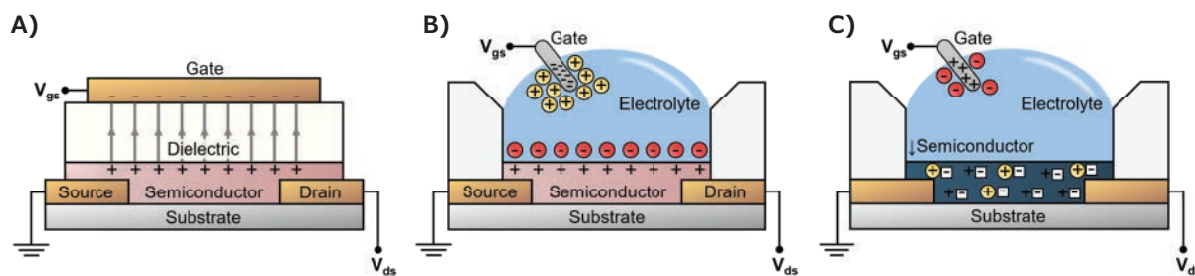


## Introduction

In our heavily industrialized world, the manufacture and disposal of electronic devices comes at a vast environmental cost. Therefore, there is a pressing need for greener electronics that thoroughly minimize environmental impact. For electronic goods, this means efficiency, sustainability, and non-toxicity at every stage of an item's lifecycle, from sourcing raw materials to the final disposal. Organic electronic devices present unique opportunities and challenges in this area. Unlike conventional silicon-based devices, organic electronics have great intrinsic potential to be environmentally friendly. This potential is rarely fully realized in the research laboratory or in devices already on the market.

An important application for organic electronics is sensing biological or chemical analytes using organic thin film transistors (OTFTs). Practical uses for OTFT sensors include health diagnostics

and monitoring, such as rapid identification of viruses to aid pandemic responses and chemical detection in industry and the environment. OTFTs are three-terminal devices where the current passing through a semiconductor between the source and drain electrodes is regulated by the voltage applied at the gate electrode. An OTFT is composed of a substrate, conductors for the electrodes, an organic semiconductor, and either an insulator or an electrolyte. **Figure 1** shows how these components are used in some common OTFT architectures. An OTFT sensor will also typically include a recognition element, such as an ion-selective membrane or enzyme, to selectively interact with a specific analyte. Sustainability and environmental concerns can be raised about each component of the device. This review will briefly consider each layer, highlighting examples of recent or noteworthy work toward improving sustainability, safety, and biodegradability.



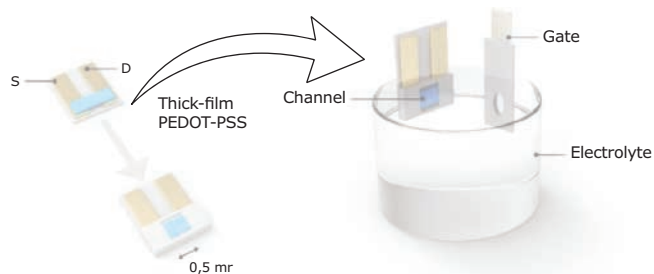
**Figure 1.** Schematics of common OTFT architectures (cross-sectional view). **A)** An organic field effect transistor (OFET), gated by a solid dielectric. **B)** An electrolyte gated OFET (EGOFET), where ions accumulate at the semiconductor boundary. Wells are often used to contain the electrolyte. **C)** An organic electrochemical transistor (OECT), where ions are injected into the semiconductor.

## Substrates

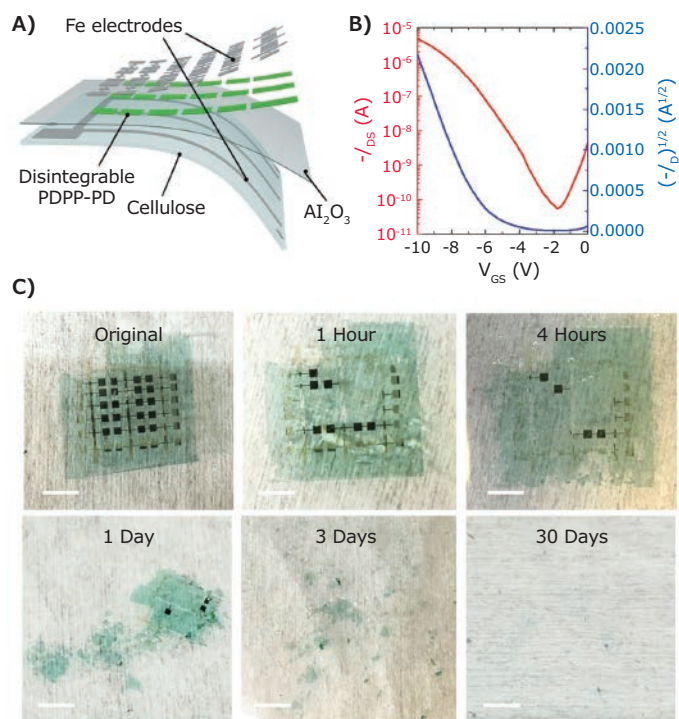
The substrate provides strength and support for the OTFT, constituting the bulk of its volume and mass and making it of critical environmental concern. In research literature, silicon wafers and glass are standard choices, but flexible polymer substrates, such as polyethylene terephthalate (PET), are also widely used. Work on greener substrates has focused on naturally sourced materials that readily biodegrade.

Paper is a feasible option for ecologically sourced, low-cost, and biodegradable alternative substrates. However, the surface properties of raw paper are rarely suited to the deposition of organic films due to the roughness and porosity of the paper. Smooth surfaces are essential for limiting the formation of defect states, thus enabling higher transistor performance.<sup>1</sup> Therefore, coatings are usually required on rough paper substrates. In one recent study, an organic electrochemical transistor (OECT) sensitive to hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was fabricated on microporous commercial photo paper (Figure 2).<sup>2</sup> In another study, a specialized paper with non-porous, hydrophilic coatings was used as the substrate for inkjet-printed organic field effect transistors (OFETs).<sup>3</sup> A downside of using coatings is that they potentially compromise the overall sustainability and biodegradability of the substrate. Sometimes, a coating can be avoided altogether.<sup>4,5</sup> Naturally derived paper coatings have also been tested for OTFT substrates, such as chitosan<sup>1</sup> (Cat. No. 419419, 448877, 448869), a biodegradable polymer derived from the shells of crustaceans. The chitosan coating dramatically improved the root mean square roughness values of the substrate, from 11.3 nm on bare paper to 2.01 nm when coated.<sup>1</sup> An important environmental consideration for any solution-processed material is the solvents used. Toxic solvents, such as halogenated compounds like chloroform, are best avoided, whereas water and alcohols are considered safer. Chitosan is exemplary in this respect, being readily dissolved in water with 2% (v/v) acetic acid (Cat. No. 338826).<sup>1</sup> It is also beneficial that few other solvents dissolve chitosan, meaning additional solution-processed layers can be deposited without risking damage to the chitosan coating.

Several other materials have also been proposed for environmentally friendly substrates. This includes standalone chitosan films,<sup>6</sup> polylactide or poly(lactic acid) (PLA, Cat. No. 38534), a thermoplastic derived from natural plant sugars,<sup>7</sup> and shellac, a resin secreted by certain insects.<sup>8</sup>



**Figure 2.** An OECT hydrogen peroxide sensor using photo paper as the substrate. Reproduced under Creative Commons license (CC BY 4.0) from reference 2, copyright 2021 American Chemical Society.



**Figure 3.** Fully disintegrable OTFTs using iron source, drain, and gate electrodes. Cellulose is used as the substrate,  $\text{Al}_2\text{O}_3$  as the dielectric, and poly(diketopyrrolopyrrole-*p*-phenylenediamine) (PDPP-PD) as the semiconductor. **A)** Device structure. **B)** Transfer characteristics. **C)** Photographs showing stages of decomposition (scale bars indicate 5 mm). Reproduced with permission from reference 9, copyright 2017 National Academy of Sciences.

## Electrodes

OTFTs often use thin metallic electrodes, which can have some drawbacks for “green” electronics. Metals are non-renewable, non-biodegradable, and challenging to extract from devices for recycling. Vacuum thermal evaporation, a common deposition method, is also very energy intensive due to the elevated temperatures and high vacuum required. Nevertheless, choosing the right metals can be beneficial. For example, fully disintegrable OTFTs have been achieved using thin iron electrodes, which rapidly disintegrate under acidic conditions (Figure 3).<sup>9</sup>

Conductive polymers, particularly poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS, like Cat. Nos. 900208, 900181, 768650, 483095), have been widely used in OTFTs in place of metallic electrodes, and offer some significant advantages. PEDOT:PSS is well known to be biocompatible and can be printed with minimal waste from water dispersions, avoiding hazards associated with toxic solvents.<sup>10</sup> Many commercial PEDOT:PSS formulations include toxic additives to enhance conductivity and stability, though concentrations of these additives are low and toxins negligible in the final films.<sup>10</sup> It is also notable that PEDOT:PSS and other conducting polymers are not considered biodegradable. The  $\pi$ -conjugated structure that is fundamental to the conductivity of these polymers makes them inert, thus, resistant to degradation.<sup>11</sup> Efforts to improve the biodegradability of conducting polymers often involve blending

conductive and intrinsically biodegradable polymers. The principle is that the biodegradable polymers will serve as a matrix for the conductive polymers and when degraded, will allow the conductive polymers to disperse. For example, non-degradable polypyrrole (PPy, **Cat. Nos. 577065, 530573**) can be combined with PLA or poly(lactic-co-glycolic acid) (PLGA) to form partially degradable blends. Alternatively, researchers have simply used much shorter conductive chains (oligomers), such as oligomers of aniline or thiophene, which are degraded more readily than polymers. A further possibility is to construct co-polymers with alternating biodegradable and conducting segments. The breakdown of the biodegradable segments breaks the polymers into smaller pieces that organisms can more readily process. For example, co-polymers can be formed using biodegradable chitosan and aniline pentamers (i.e., strings of five aniline units).<sup>11</sup> Such approaches have had minimal use in OTFT electrodes to date.

## Insulators and Electrolytes

Substantial work has been done towards finding environmentally friendly and naturally sourced dielectric materials for OTFTs. We will discuss a few interesting examples.

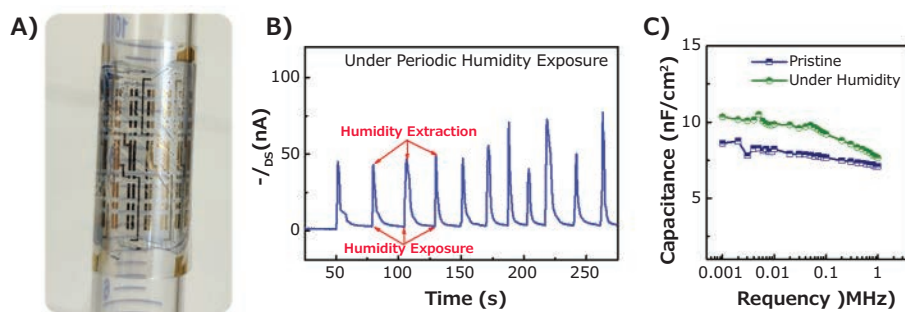
Polypropylene carbonate (PPC) is a material synthesized from carbon dioxide (CO<sub>2</sub>) and propylene oxide and is often considered to be a more environmentally friendly polymer. PPC sequesters captured CO<sub>2</sub> and is synthesized without using organic solvents or producing organic waste. It is also enzymatically biodegradable. PPC has been demonstrated as an effective dielectric for both p-type and n-type OFETs, as well as serving as a flexible substrate.<sup>12</sup> While promising, it should be noted that PPC is not wholly “green.” The precursor, propylene oxide, is a toxin and carcinogen originating from non-renewable petroleum.<sup>13</sup> For these reasons, many researchers have preferred naturally sourced dielectric materials.

One promising natural dielectric is almond gum, a polysaccharide produced by almond trees. Almond gum is nontoxic, biodegradable, and water soluble. In a 2020 study, the authors used fresh almond gum with minimal processing. The material was dissolved

in distilled water and coated via spray pyrolysis. OFETs using almond gum dielectric layers exhibited good, low-voltage (<3 V) characteristics.<sup>14</sup> Another natural and biodegradable dielectric is gelatine (**Cat. No. 1.04078**), a protein extracted from the bones, skin, and other tissues of animals used in the livestock industry. In one study, gelatine films were spin-coated from an aqueous solution and used in flexible OFETs. The OFETs were responsive to changes in humidity, where device performance improved with greater moisture content, owing to an increase in capacitance due to the mobilization of ions in the gelatine layers (**Figure 4**).<sup>15</sup>

A recent development is the use of crosslinked dextran (**Cat. No. 31430**), a natural polymer that fungi can decompose. The authors of this study note that many previously reported biodegradable dielectrics, including cellulose (**Cat. No. 433837**) and chitosan, are polar and hydrophilic, meaning they are affected by ambient moisture and induce charge trapping. While such properties are potentially useful in devices such as humidity sensors, as seen above, this behavior is usually unwanted. The cross-linking of dextran reduces its polar hydroxyl groups, enabling stable, high-performance OFETs. The full device, where the dextran dielectric doubles as a substrate, was observed to disappear within 67 hours of contact with fungi grown on decomposing peaches. The non-biodegradable components (including gold electrodes) were broken up and dispersed.<sup>16</sup>

Not all OTFTs rely on conventional dielectric layers. OECTs (organic electrochemical transistors) and electrolyte gated OFETs (EGOFETs), which are widely used as sensors, replace the dielectric with electrolytes that allow low-voltage operation. Electrolytes can be as simple as salt water. In some sensing applications, the fluid under analysis serves as the electrolyte. In these cases, the environmental impact of the electrolyte is negligible. One limitation of liquid electrolytes is that they require additional structures to contain or encapsulate them, which can be bulky and add to fabrication complexity. To achieve very thin, self-contained EGOFETs and OECTs (organic electrochemical transistors) with no risk of leaking or spilling, solid-state electrolytes are sometimes preferable. However, many reported



**Figure 4:** A) OFET array with gelatine dielectric, wrapped around a glass tube to show its flexibility. B) The drain-source current of the gelatine OFET under periodic exposure to humid air. C) Exposure to humidity increases the capacitance of the gelatine layer. Reproduced with permission from reference 15, copyright 2020 American Chemical Society.

solid electrolytes are not biodegradable or biocompatible. In one recent report, a solid, biodegradable electrolyte composed of Levan polysaccharide and a choline-based ionic liquid was used in a hybrid EGFET/OECT device.<sup>17</sup> The choline-based ionic liquid was formed by reacting choline with malic acid, resulting in a liquid with choline cations and malate anions. After mixing with an aqueous solution of the Levan polysaccharide, the material was cast as a freestanding film and used as both substrate and dielectric. Metal electrodes (chromium and gold) were thermally evaporated and the biocompatible semiconductor poly[3-(5-carboxypentyl)thiophene-2,5-diyl] (P3CPT) was spin-coated onto polydimethylsiloxane (PDMS, **Cat. Nos. 482145, 480282, 433012, 481696**) and subsequently transferred to the electrolyte. Biocompatibility was demonstrated by subcutaneously implanting the device into rats. The device was decomposed within seven days *in vivo*. The transistors successfully measured electrocardiogram signals on human skin and rat hearts.<sup>17</sup>

## Semiconductors

The active layer of an OTFT, the organic semiconductor, has been comparatively overlooked in efforts to find greener materials for OTFTs. Many of the most common organic semiconductors in use are biocompatible but show limited biodegradability and rely on toxic solvents for solution processing. Nevertheless, some good progress has been made.

Indigo is a natural dye that has long been used as food colorings and textile dyes, exhibiting low toxicity and good biodegradability.<sup>18</sup> Indigo derivatives can be synthesized for optimized semiconductor characteristics; many variations have been tested in OTFTs. In one paper, OFETs were fabricated using a variety of indigo derivatives, including 6,6'-dichloroindigo and 5,5',6,6'-tetrafluoroindigo. Depending on the added functional groups, these displayed a range of n-type and ambipolar charge transport characteristics. However, the indigo films were deposited via vacuum thermal evaporation due to their poor solubility. Another limitation of these organic semiconductors was their poor stability in air.<sup>18</sup>

A decomposable conjugated polymer was synthesized from the naturally derived and degradable monomer diketopyrrolopyrrole (DPP) in another study. The monomers were linked with imine bonds, which break down in mild acid.<sup>9</sup> Biocompatibility of the new polymer was demonstrated with *in vitro* cell culture tests. Transistors made using this material exhibited “nearly ideal” transistor characteristics, with good hole mobilities, on/off ratios, and air stability. Flexible devices were made using this polymer, combining cellulose substrates with dissolvable iron electrodes, as mentioned earlier, to create fully degradable devices (**Figure 2**).<sup>9</sup>

## Recognition Elements

The components reviewed thus far apply to OTFTs in general. In OTFT sensors, a recognition element is also typically required to facilitate selective interaction with an intended ion or molecule. As with all other transistor components, environmental impacts relating to the recognition element must be considered.

In many cases, the recognition element is a naturally occurring molecule, such as an enzyme or antigen, that is immobilized onto an active surface of the transistor, such as the gate electrode. For example, an OECT sensor for COVID-19 antibodies has been demonstrated.<sup>19</sup> A person infected with SARS-CoV-2 will produce antibodies that bind to a specific antigen associated with the virus, such as the spike protein. The presence of antibodies indicates past or present infection. To detect antibodies using an OECT, spike proteins from the virus were chemically bound to a self-assembled monolayer of mercaptoacetic acid on the gold gate electrode of the transistor. The positive charge of the antibodies causes a shift in the effective gate voltage of the device.<sup>19</sup> In this case, the antigen itself is a natural protein that will degrade under normal conditions, posing no environmental threat. However, further investigation would be needed to assess the monolayer and electrode.

To achieve ion selectivity in OTFTs, it is common to use an ion-selective membrane, which is also widely used in potentiometric ion-selective electrodes. The membrane is typically made using plasticized polyvinyl chloride (PVC, **Cat. Nos. 81388, 81392**) embedded with ionophores, which selectively bind with a specific ion, changing the membrane potential. More environmentally friendly alternatives to PVC have been explored, including PLA.<sup>20</sup> PLA is a sustainable, plant-derived thermoplastic used as 3D printing feedstock that is considered biodegradable under certain conditions. To make a PLA membrane, plasticized PLA was combined with an ionophore and extruded into 3D printing filament. The membranes could then be printed into the desired shape using a conventional, consumer-grade 3D printer. The 3D printed membranes were demonstrated in an electrochemical cell to detect Hg<sup>2+</sup> concentration in water.<sup>20</sup> While this approach to producing environmentally friendly ion-selective membranes would be straightforwardly transferrable to OTFT sensors, this has not yet been reported.

## Conclusions

In this brief review, we have seen examples of how a careful choice of materials can significantly reduce the environmental impact of each principal component of OTFT sensors. A considerable amount of essential and innovative work has already been done, but progress has yet to be uniform in every area. It is also clear that many of these developments have been demonstrated in isolation. Few reports show complete devices that are wholistically ecological, non-toxic, and safely degradable for each component. Further work is therefore needed to integrate the many existing insights together into fully eco-friendly OTFT sensors. In attempting this, an ongoing challenge will be to achieve the device performances needed to compete with current state-of-the-art devices. We hope this will drive further innovation. Finally, we have observed several places where a proposed material, while promising great environmental benefits in one aspect, may have notable weaknesses in other areas. Such work should still be encouraged. Even partially “green” electronics may have tangible benefits as we work toward a sustainable future. Nevertheless, caution and skepticism are warranted with claims of environmental friendliness.







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## Organic Semiconductors

## Organic Hole Transport Materials (p-type)

| Name  | Description  | Orbital Energy                 | Cat. No. |
|---|--|--------------------------------|----------|
| N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine                             | 99%  | HOMO 5.5 eV<br>LUMO 2.3 eV     | 443263   |
| 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl  | 97%  | HOMO 6 eV<br>LUMO 2.9 eV       | 660124   |
| 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl  | 99.9% trace metals basis   | HOMO 6 eV<br>LUMO 2.9 eV       | 699195   |
| N,N'-Diphenyl-N,N'-bis-[4-(phenyl-m-tolylamino)phenyl]biphenyl-4,4'-diamine | 95%  |                                | 900968   |
| J51   | M <sub>w</sub> 40,000-80,000 by GPC (PS standard)                                      | HOMO -5.29 eV<br>LUMO -3.3 eV  | 901058   |
| J61   | M <sub>w</sub> 50,000-100,000 by GPC (PS standard)                                     | HOMO -5.22 eV<br>LUMO -3.21 eV | 901045   |
| Me-4PACz  | ≥98%   | HOMO -5.74 eV<br>LUMO -2.49 eV | 923184   |
| PBDB-T  | M <sub>w</sub> >50,000 by GPC (GPC standard: PS)                                       | HOMO -5.28 eV<br>LUMO -3.48 eV | 901099   |
| PBDTTT-C-T  | ≥99% trace rare earth metals basis<br>M <sub>w</sub> 80,000-150,000 (GPC, PS standard) | HOMO -5.11 eV<br>LUMO -3.25 eV | 901067   |
| PDBT-T1   | M <sub>w</sub> 20,000-50,000 (GPC, PS standard)  | HOMO -5.36 eV<br>LUMO -3.43 eV | 901097   |
| PDPP2T-TT-OD  | average M <sub>w</sub> 40,000-60,000 by GPC  | HOMO 5.2 eV                    | 791989   |
| PfBT4T-C9C13  | M <sub>w</sub> 35,000-100,000  | HOMO -5.34 eV<br>LUMO -3.69 eV | 900980   |
| Poly(3-hexylthiophene-2,5-diyl)   | average M <sub>w</sub> 50,000-100,000  | HOMO 5 eV<br>LUMO 3 eV         | 445703   |
| Poly(9,9-dioctylfluorenyl-2,7-diyl)   | M <sub>w</sub> 50,000-150,000 by GPC   | HOMO -5.3 eV<br>LUMO -2.8 eV   | 923214   |
| Poly(9,9-dioctylfluorenyl-2,7-diyl) end capped with dimethylphenyl          | M <sub>w</sub> 50,000-150,000 by GPC   | HOMO -5.3 eV<br>LUMO -2.8 eV   | 923222   |
| Poly-TPD  | M <sub>w</sub> ≥20,000 g/mol   | HOMO -5.2 eV<br>LUMO -2.4 eV   | 907065   |
| PTAA  | average M <sub>n</sub> 7,000-10,000 (GPC)  |                                | 702471   |
| PTB7  | average M <sub>w</sub> 80,000-200,000  | HOMO -5.15 eV<br>LUMO -3.31 eV | 772410   |
| SHT-263 Solarpur®   | ≥99.9%   |                                | 902500   |
| SHT-263S Solarpur®  | ≥99%   |                                | 916021   |
| Silicon tetrabiphenyl MeOTAD  |  | HOMO -5.34 eV<br>LUMO -2.30 eV | 924385   |
| Spiro-MeOTAD  | 99% (HPLC)   |                                | 792071   |

| Name                             | Description  | Orbital Energy                 | Cat. No. |
|----------------------------------|--|--------------------------------|----------|
| 2,4-Spiro-OMeTAD                 |  ≥99% (HPLC)                  | HOMO -5.24 eV<br>LUMO -2.08 eV | 923230   |
| Spiro-TTB                        |  ≥99% (HPLC)                  | HOMO 5.2 eV<br>LUMO 1.9 eV     | 923192   |
| TFB                              |  average $M_w$ >30,000 by GPC |                                | 901101   |
| 1,3,5-Tris(diphenylamino)benzene |  97%                          |                                | 663247   |

### Organic Electron Transport Materials (n-type)

| Name          | Description  | Cat. No. |
|---------------|--|----------|
| Bathocuproine |  96%                        | 140910   |
| Bathocuproine |  99.99% trace metals basis  | 699152   |
| B3PYMPM       |  ≥99% (sublimed)            | 900958   |
| BPy-TP2       |  ≥99% (sublimed)            | 900939   |
| Liq           |  >99.5% (sublimed, HPLC)    | 900928   |
| PFN-Br        |  $M_w$ 30,000-50,000 by GPC | 906980   |
| TBPe          |  99% (sublimed, HPLC)       | 900937   |
| 3TPYMB        |  ≥98%                       | 900953   |

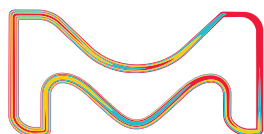
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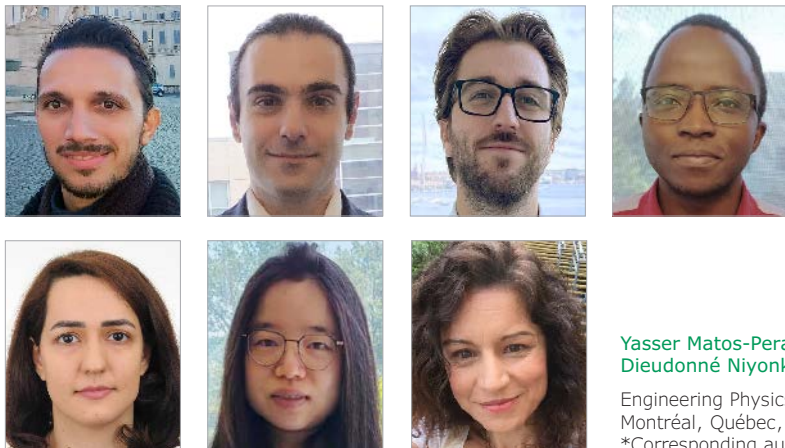
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# Nature as the Source of Materials for More Sustainable Organic Electronics



Yasser Matos-Peralta, Manuel Reali, Anthony Camus, Dieudonné Niyonkuru, Molood Hoseinsizadeh, Zhaojing Gao, Clara Santato\*

Engineering Physics, Polytechnique Montréal, 2900 Boulevard Edouard Montpetit, Montréal, Québec, H3T 1J4, Canada.

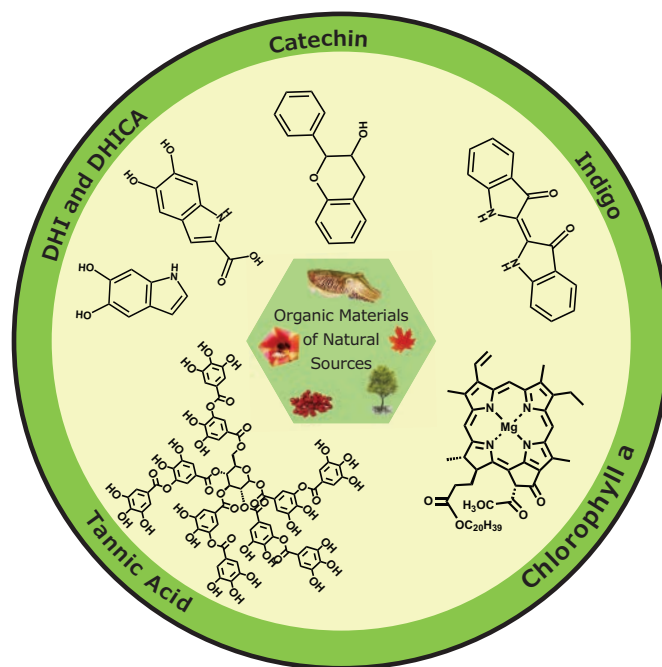
\*Corresponding author: clara.santato@polymtl.ca

## Introduction

The need for eco-friendly technologies is the underpinning of Sustainable Organic Electronics (SOE) and their powering elements.<sup>1</sup> SOE uses carbon-based electronically conjugated (i.e., featuring alternance of single and double carbon-carbon bonds) molecular materials extracted from natural sources (bio-sourced) or synthesized along the principles of “green” chemistry.<sup>2,3</sup> To limit the device embodied energy (i.e., the energy associated with device manufacturing, including energy for extracting, refining, processing, and transporting primary materials), materials for SOE are usually solution-processed (e.g., printed electronics). SOE is meant to limit the use of critical chemical elements used in conventional electronics.<sup>4,5</sup> Further, organic electronic materials and devices can be eco-designed for biodegradation at their end-of-life, thus helping to alleviate the accumulation of Waste of Electrical and Electronic Equipment (WEEE or e-waste, summing up to 53.6 Mt at the global level in 2019, equivalent to 4500 Eiffel towers).<sup>1,5</sup>

Indigoids, melanins, chlorophylls, and tannins are examples of bio-sourced materials under investigation in SOE<sup>6-8</sup> (Figure 1), where DHI and DHICA are the building blocks of eumelanin, the black-brown form of melanin, and catechin and tannic acid belong to the tannin family of molecules. For instance, tannins can be extracted from forest residues and agricultural biomass waste. They can also be obtained as by-products of the food industry.

In organic materials, the weak van der Waals intermolecular interactions (ca. 0.4-4 kJ/mol, 4 to 40 meV per chemical bond) cause structural and energetic disorder that affect the mechanism of electronic transport in the materials and, consequently, the performance of devices based thereon. Structural disorder can be caused by the twist of molecular backbones, longer (or



**Figure 1.** Molecular structures of interest in SOE: chlorophyll a, tannic acid, 5,6-dihydroxyindole (DHI), 5,6-dihydroxyindole-2-carboxylic acid (DHICA), catechin, and indigo.

shorter)-than-average conjugation lengths, molecular chains not arranged in periodic structures, or the existence of  $\pi$ - $\pi$  stacked regions with different extensions and orientations.<sup>9</sup> Today, various transport models are proposed, but they have certain limitations and a universal model has not yet been developed.<sup>10</sup>



## Challenges With Bio-sourced Organic Semiconductors

Charge carriers in organic semiconductors (OSCs) feature lower mobility (typically  $10^{-1}$ – $10^{-5}$   $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) than their inorganic counterparts.<sup>11</sup> Most natural and synthetic OSCs suffer from high structural disorder because of weak intermolecular van der Waals interactions holding the molecules together in films amenable to devices. This causes short-range-electron delocalization, a limiting factor for electronic transport.<sup>12</sup> Open challenges in the OSCs field are their poor environmental (shelf life) operational stability and limited multifunctionality, e.g., the possibility to combine efficient transport and electroluminescence as needed in organic light-emitting organic transistors.

Concerning device stability, Organic Field Effect Transistors (OFETs) based on hydrogen-bonded air-stable organic semiconductors, such as indigo and Tyrian purple, reached mobility in the range of  $0.01$ – $2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ .<sup>4,13</sup> Quinones are small organic molecules ubiquitous in nature that contain two adjacent (or separated) carbonyl groups in an unsaturated six-carbon ring structure; quinone derivatives (i.e., anthraquinones AQ, benzoquinones BQ, *N*-heteropentacenequinones HAQ, quinacridones QA) are among the most interesting hydrogen-bonded semiconductors.<sup>4</sup>

Owing to the structural disorder of bio-sourced materials of interest in organic electronics, it is difficult to know the position of their HOMO and LUMO energy levels since the structural disorder implies energetic disorder. Only very recently, studies by ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) gave insight into the LUMO and HOMO levels of building blocks of the biopigment eumelanin, i.e., 5,6-dihydroxyindole of (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA).<sup>14</sup> The need to understand the energy levels poses a challenge to engineering efficient metal electrode/organic material device interfaces, for example, when minimizing the charge carrier injection (Schottky) barrier. The Schottky barrier is the energy offset between the Fermi level of the metal electrodes and the HOMO and LUMO levels of the material. One-dimensional carbon nanotube (CNT)-based electrodes offer the opportunity of efficient charge carrier injection due to favorable electrostatic effects, which permits circumvention of injection barriers.<sup>15,16</sup>

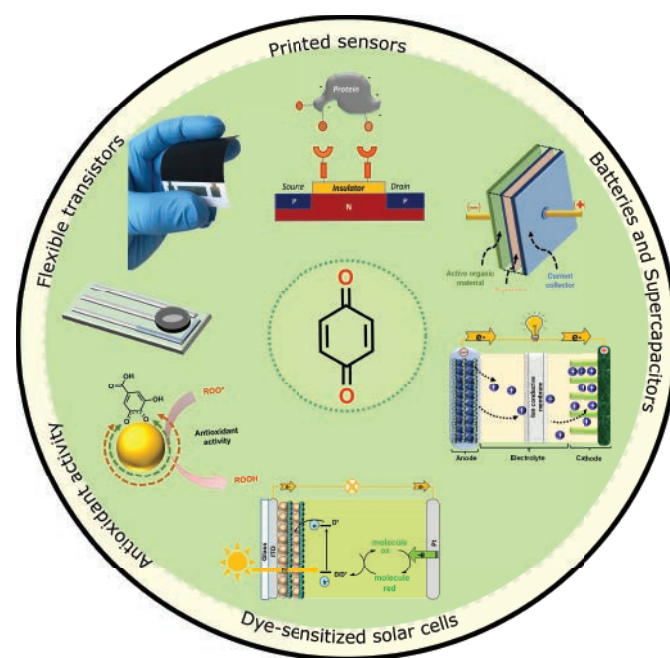
## Powering Elements for SOE: Energy Conversion and Storage

Quinone-based materials are promising for applications in renewable energy, such as solar energy conversion and electrochemical energy storage.<sup>7</sup> Quinones feature varying redox states: fully oxidized quinones, semiquinones, and reduced hydroquinones. In aqueous solutions, quinones undergo two-electron, proton-coupled electron transfers. Furthermore, quinones show high metal ion binding affinity, e.g., through chelation and/or electrostatic interactions. Such affinity is relevant in electrochemical energy storage devices that rely on mixed ionic and electronic transport, such as batteries and supercapacitors.<sup>7</sup> It is worth noting that

the metal ion binding affinity also permits metal recovery and separation for water purification and e-waste treatment applications by biohydrometallurgy techniques.<sup>17</sup> Other properties of quinones include antioxidant activity and medicinal chemistry.<sup>18</sup>

Quinones-based biopigments, such as melanins and tannins, have been applied in batteries and electrochemical capacitors (supercapacitors). We have reported on supercapacitors based on carbon paper electrodes, surface-modified by solution-processed melanins or tannins.<sup>19,20</sup> To tackle challenges such as poor electronic coupling between the quinone-based material and the current collectors and low cycling stability (i.e., loss of capacitance over long charging/discharging cycling), we chemically treated the carbon paper in a way to improve electrolyte wettability, enhance the surface area, and tailor surface porosity.<sup>20</sup> Quinones in electrochemical systems can feature their poor electrical conductivity. Here, the supramolecular organization plays a vital role in the quinone-based materials. Theoretical studies can guide the engineering of such organization.<sup>21,22</sup> Furthermore, to limit the release of the quinones by solubilization into electrolytes, it is helpful to use semi-solid-state electrolytes such as ion gels that also bring mechanical integrity to the devices. Semi-solid-state electrolytes that feature ionic mobility and mechanical flexibility are a combination of polymers such as poly(ethyl oxide) (PEO, like **Cat. Nos. 372781, 182028, 372773**) or poly(vinyl alcohol) (PVA, **Cat. No. 360627**), with salts such as NaCl,  $\text{MgCl}_2$ , and  $\text{Na}_2\text{SO}_4$ .<sup>23</sup>

Quinones-based materials can feature high UV-Vis absorption, suitable for light-assisted electrochemical energy storage and solar energy conversion applications, e.g., dye-sensitized photoelectrochemical cells.<sup>7,21,24</sup> (See **Figure 2**).



**Figure 2.** Technological applications making use of quinone-based materials.

## Printing

The fabrication of films and devices through printing is of primary importance in developing sustainable organic electronic devices. Printing is an additive process that offers the possibility to i) reduce the waste of materials,<sup>25</sup> ii) reduce the energy required to fabricate a device,<sup>26</sup> iii) reduce the overall manufacturing cost, and iv) fabricate flexible devices. Moreover, printing is a scalable technology that can provide a high manufacturing throughput (e.g., gravure printing and flexography up to  $10^2 \text{ m}^2 \text{ s}^{-1}$ ).<sup>27</sup>

Among various industrial printing technologies, gravure printing, reverse offset, and inkjet printing are promising in terms of scalability, printing speed, and spatial resolution. Printing technologies are rapidly evolving and can achieve printed feature sizes down to a few microns (as well as down to sub-microns).<sup>25,28</sup>

The formulation of inks consists of combining semiconducting (e.g., Cat. Nos. **923184**, **923222**, **924385**, **923230**, **923192**, **902012**, **900958**, **906980**) or conducting (e.g., Cat. Nos. **923567**, **923575**, **923559**, **900208**, **900181**, **793663**, **900695**, **900960**) active materials with solution processable polymer binders. Blended inks are two-phase systems (polymer matrix/active material), possibly forming percolating networks for charge carriers.<sup>29</sup>

Bio-sourced materials (extracted from natural sources) can benefit from printing technologies. Insulating natural polymers like Shellac (*Kerria lacca*) can be used as a biodegradable binding agent to formulate ink blends.<sup>29</sup> Nanostructured bio-sourced materials featuring compelling charge carrier transport properties but poor solution processability, such as Sepia melanin (e.g., extracted from the ink sac of *Sepia officinalis*), could take advantage of the protecting and stabilizing properties of binders.<sup>30</sup>

It is worth mentioning that one of the biggest challenges in printing technologies is related to the sustainability of the solvents used. Many of the utilized solvents are based on toxic volatile organic compounds (VOCs) that are environmental pollutants. Therefore, it is necessary to search for more ecological solvent solutions. However, substituting a solvent for an eco-friendlier one is a challenging task. It should be considered that the new solvent must dissolve the solutes and allow adequate ink-substrate wetting, ink-film formation, and correct drying of solute-film during the printing/coating process.<sup>31</sup> Generally, water is the ideal greener solvent to use in this process. Still, it is necessary to consider solute affinity because various organic molecules and polymers are not soluble in water. Other greener solvents to consider are alcohols and mixtures of alcohols (e.g., 1-propanol, isopropanol Cat. No. **190764**), anisole (Cat. No. **296295**), ethoxybenzene (Cat. No. **241989**), and *N,N'*-dimethylpropyleneurea (Cat. No. **241569**).<sup>32</sup>

## Biodegradation

Biodegradation of devices at their end-of-life is one of the critical challenges in developing sustainable organic electronic devices. We wish to point out that being organic, bio-sourced does not mean automatically to be biodegradable.<sup>33,34</sup> When biodegradation happens in compost conditions (it is worth mentioning that biodegradable organic devices have also been investigated for biomedical technologies<sup>35</sup>), the molecular and supramolecular structures of some bio-sourced organic molecules and polymers can cause recalcitrance to microbial attack during the degradation. Aspects such as humidity, pH, temperature, and solar illumination must be considered to gain insight into factors promoting or inhibiting biodegradation.<sup>2,17,34</sup> It is worth noting the possible (eco)toxicity of chemical intermediates in the biodegradation process (i.e., the biodegradation process should be continuously monitored to characterize chemical intermediates). Sustainable organic electronics is a research area still in its infancy, such that biodegradability tests are not yet standardized. Compostability tests for conventional (insulating) plastics are CAN/BNQ 0017-088/2010, ASTM D6400, EN 13432, and EN 14995.<sup>17,33</sup> As an example of biodegradability study for sustainable organic electronics, our study related to the biodegradation of eumelanin in mesophilic and thermophilic conditions employed the ASTM D5338 standard test for the aerobic biodegradation of plastic materials under controlled composting conditions.<sup>33</sup>

## Conclusions and Perspectives

The dramatic impact of electronics on the environment and human health requires a paradigm shift from linear to circular electronics. Here, we indicate responsible and respectful use of resources, responsible manufacturing practices, and practical electronic end-of-life management. To realize such a shift, eco-design of electronics and extended producer responsibility should be at the core of all related efforts.










We believe several responses are needed to develop sustainable electronics tailored to consumers' needs and local constraints. For efficient composting, engineering of the microbiota should be pursued due to possible traces of device metal contacts acting as biodegradation inhibiting agents. Additionally, the conductivity of carbon-based contacts is usually lower than that of conventional metals-based counterparts (e.g., Au). Disassemblable (modular) devices, wherein metal contact-patterned substrates can be reused, could offer a viable solution.

As in other industrial sectors, waste should be a keyword. E-waste is an opportunity, such as the recovery of precious metals in the recycling process. The concept of waste should evolve; it should be seen as a step in the life of materials to be used to produce new materials. Organic electronic materials offer a possibility to alleviate the impact of electronics on the environment and human health for several reasons: they are based on carbon, an abundant element, and they can be printed for low-embodied-energy devices. End-of-life scenarios for these materials, such as composting, can easily be foreseen.

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## Biosourced Solvents for Electronic Applications












| Name  | Relative Evaporation Rate  | Hansen Dispersion | Solubility Polar | H Bonding Parameter | Cat. No. |
|---|--|-------------------|------------------|---------------------|----------|
| ElectroGreen™, Acetone substitute for electronics, bio-sourced            |  2.84   | 7.7               | 3.4              | 6.1                 | 929670   |
| ElectroGreen™, Butyl Cellosolve substitute for electronics, bio-sourced   |  0.11   | 7.5               | 3.8              | 6.1                 | 929697   |
| ElectroGreen™, Cyclohexanone substitute for electronics, bio-sourced      |  0.25   | 7.7               | 3.5              | 6.4                 | 929735   |
| ElectroGreen™, Isopropyl Alcohol substitute for electronics, bio-based    |  1.24   | 7.7               | 4.2              | 8.8                 | 929654   |
| ElectroGreen™, Methyl Amyl Ketone substitute for electronics, bio-sourced |  0.247  | 7.7               | 3.4              | 6.7                 | 929727   |
| ElectroGreen™, NMP substitute for electronics - type 1, bio-sourced       |  < 0.05 | 8.8               | 5.9              | 3.7                 | 929719   |
| ElectroGreen™, NMP substitute for electronics - type 2, bio-sourced       |  < 0.02 | 9                 | 6.8              | 4.6                 | 929662   |
| ElectroGreen™, Toluene substitute for electronics, bio-sourced            |  2.57   | 7.7               | 2.8              | 6                   | 929689   |
| ElectroGreen™, Xylene substitute for electronics, bio-sourced             |  0.89   | 7.7               | 3.1              | 5.8                 | 929700   |

## Semiconducting Materials

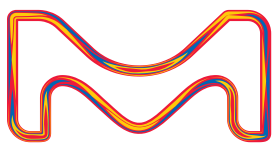
### Singlewalled Carbon Nanotubes

| Name  | Description   | Form  | Cat. No.      |
|---|---|---|---------------|
| Carbon nanotube, single-walled                                      |  (7,6) chirality, ≥90% carbon basis (≥77% as carbon nanotubes), 0.83 nm average diameter | powder (freeze-dried)                         | <b>704121</b> |
|   |  98% (Semiconducting)  | solid   | <b>750522</b> |
|   |  (6,5) chirality, ≥95% carbon basis (≥95% as carbon nanotubes), 0.78 nm average diameter | powder (freeze-dried)                         | <b>773735</b> |
| Carbon nanotube, single-walled, carboxylic acid functionalized      |  >90% carbon basis, D × L 4-5 nm × 0.5-1.5 μm , bundle dimensions                        | powder  | <b>652490</b> |
| Carbon nanotube, single-walled, conductive aqueous ink              |  SWCNT 0.2 mg/mL   | dispersion in H <sub>2</sub> O (black liquid) | <b>791490</b> |
|   |  0.9-1.1 g/L (SWCNT concentration by Absorbance at 854 nm)                               | dispersion in H <sub>2</sub> O (black liquid) | <b>791504</b> |
| Carbon nanotube, single-walled, solvent-based conductive ink, SWCNT |  1 mg/mL   | viscous liquid (black)                        | <b>792462</b> |

### Inorganic Inks

| Name                        | Description   | Particle size | Cat. No.      |
|-----------------------------|---|---------------|---------------|
| Boron nitride               |  nanoplatelet, 0.1-0.5 mg/mL in H <sub>2</sub> O | ≤500 nm       | <b>900710</b> |
|                             |  nanoplatelet, 20 mg/mL in H <sub>2</sub> O      |               | <b>900417</b> |
| Hexagonal boron nitride ink |  for blade coating                               | ≤0.3 μm       | <b>901349</b> |
|                             |  for inkjet printing                             | ≤0.3 μm       | <b>901410</b> |
| Molybdenum disulfide        |  dispersion, 0.1-0.5 mg/mL in H <sub>2</sub> O   | ≤500 nm       | <b>900724</b> |
|                             |  suspension                                      |               | <b>902012</b> |
|                             |  ink for inkjet printing                         | ≤0.4 μm       | <b>901187</b> |
|                             |  ink for spin/spray coating                      | ≤0.4 μm       | <b>901867</b> |
|                             |  suspension                                      |               | <b>901797</b> |
| Molybdenum oxide            |  nanoparticle ink                                | 10-40 nm      | <b>900151</b> |
| Zinc oxide ink              |  for inkjet printing                            |               | <b>901091</b> |





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# Substrate and Conductor Materials Towards More Sustainable Electronics



Liisa Hakola, Henrik Sandberg, Maria Smolander\*

VTT Technical Research Centre of Finland Ltd., Espoo, Finland  
\*Email: maria.smolander@vtt.fi

## Introduction

E-waste accumulation poses an escalating issue for society as end-of-life electronics are not circulated, recycled, or managed efficiently. At the same time, the accelerating consumption of raw materials threatens the availability of limited resources. The European Green Deal and Circular economy action plan work to address these challenges through ecological products and increased circulatory work. Additionally, the EU (European Union) Ecodesign Directive is being revised beyond currently emphasized energy efficiency practices to support a full circular economy, including the use of natural resources by maximizing their value and minimizing their waste. Both plans seek to improve the circularity of raw material, substrates and active materials via manufacturing methods, circular design, and eco-design principles (such as efficient recovery processes). In this mini review, we will highlight the possibilities of renewable substrates and conductive materials, with particular attention paid to flexible electronics.

## Towards Sustainable Substrates

Electronic products are usually fabricated on fossil fuel-based substrates, such as plastic composite FR4 or plastics like polyimide (Cat. No. **GF77686521**) or polyethylene terephthalate (PET, Cat. Nos. **GF09063581**, **GF25214475**, **GF32099272**, **GF48528591**, **GF89357619**). These are characterized according to process compatibility and suitability for varying application requirements, such as elevated temperature, humidity tolerance, and fire retardancy. However, these substrates have a high environmental impact due to reliance on non-renewable raw materials, limited recyclability, and excess material consumption (thicknesses, etc.). More ecological substrate alternatives for electronics can be found among cellulose and wood-based materials, such as paper-based products,<sup>1</sup> and bioplastics, such as poly lactic acid (PLA, Cat. Nos. **764620**, **764612**, **767344**).<sup>2</sup> Silk fibroin, nanocellulose, and nanochitin are also

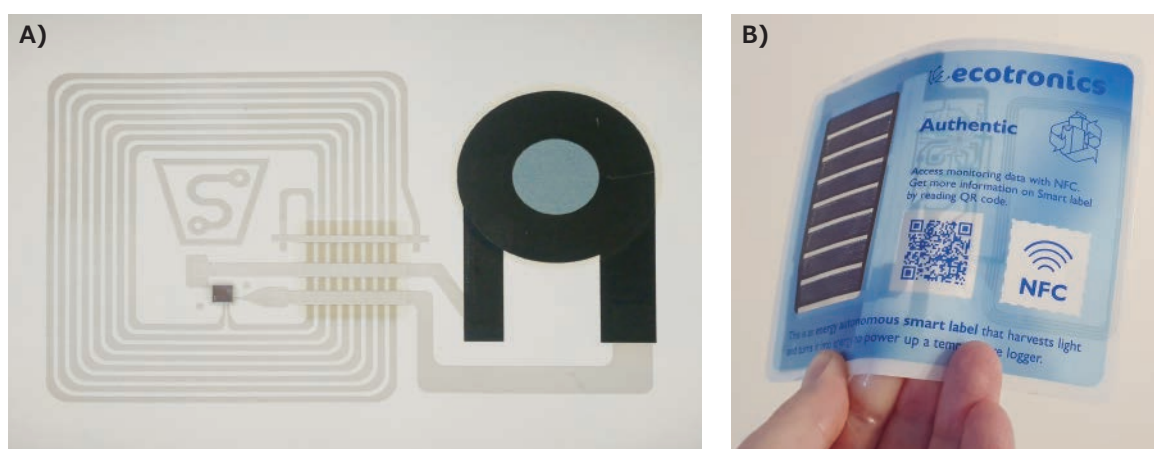
referenced resources.<sup>3,4</sup> Although these materials do not possess as good fire retardancy as traditional electronic substrates, their properties can be improved with special coatings, such as bio-based fire retardants.<sup>5</sup> These substrate materials are thin and flexible and, therefore, compatible with sustainable printing-based manufacturing processes that require lower material and energy consumption than etching-based processes.<sup>6,7</sup> However, electric functionality demands specific parameters for surface roughness and adhesion, mechanical durability, temperature stability, moisture tolerance, and eco-friendly substrate alternatives can face challenges in meeting these targets. Biodegradability is a desirable property of printed electronics used in applications that terminate in a natural environment. Immonen et al.<sup>5</sup> have shown that wood and paper-based substrates have a relative biodegradability between 33–52% (compared to a microcrystalline cellulose standard). In contrast, biopolymer substrates can have an even higher degradation rate.<sup>19</sup> Fossil-based and bio-based electronic substrates are compared in **Table 1**.

Paper-based substrates have advantageous characteristics, such as low-cost, flexibility, biodegradability, recyclability, deformability, and thermal stability. For printed electronics where smooth, dimensionally stable, and non-absorbing substrates are optimal for achieving targeted functionality, complications might stem from high roughness, absorbency, poor barrier properties, and moisture sensitivity. Some of these obstacles can be overcome by using coatings, fillers, and additives to increase surface smoothness, reduce the size of the pores, improve paper strength, and optimize printability with functional inks.<sup>8–12</sup>

In printed electronics paper-based substrates have been used to manufacture many types of devices and components, such as thermochromic and electrochromic displays, resistive memory

**Table 1.** Properties of the most common and emerging electronic substrates.<sup>1,5,19</sup>

|                                | FR4                          | Polyimide          | PET                                 | Biopolymer films                                | Cellulose based             |
|--------------------------------|------------------------------|--------------------|-------------------------------------|---|-----------------------------|
| <b>Flexibility</b>             | No                           | Yes                | Yes                                 | Yes   | Yes                         |
| <b>Price</b>                   | Low                          | Medium             | Medium                              | High  | Low                         |
| <b>Thermal resistance</b>      | Medium (thermal index 140°C) | Good (up to 200°C) | Medium ( $\leq 120^\circ\text{C}$ ) | Medium ( $\leq 140^\circ\text{C}$ )             | Good (at least momentarily) |
| <b>Moisture resistance</b>     | Good                         | Good               | Good                                | Good  | Poor                        |
| <b>Roughness</b>               | Low                          | Low                | Low                                 | Low to medium                                   | Medium to high              |
| <b>Renewable raw materials</b> | No                           | No                 | No                                  | Yes   | Yes                         |
| <b>End-of-life</b>             | Landfill or burning          | Plastic recycling  | Plastic recycling                   | Plastic recycling / Compostable / Biodegradable | Recycling / Biodegradable   |



**Figure 1.** Examples of electronic devices on sustainable substrates: **A)** anti-counterfeit label consisting of printed electrochromic display and Near Field Communication (NFC) antenna on paper substrate. Reprinted with permission from reference 20, copyright 2018 American Chemical Society and **B)** energy autonomous temperature logger based on a printed Organic Photovoltaic (OPV) panel and a supercapacitor, and NFC communication on bio-plastic PLA substrate. Reprinted with permission from reference 25, copyright 2016 MDPI.

devices, transistors, capacitors, disposable radio frequency identification (RFID) tags, smart labels for intelligent packaging, batteries, photovoltaic cells, diagnostics, and sensors and actuators.<sup>13-16</sup> Wearable devices, such as pressure sensors, thermoelectric generators, and smart bandages, are advancing applications thanks to the high breathability of paper-based materials. It is calculated that with respect to Life Cycle Assessment (LCA) categories, such as global warming potential, water use or eutrophication, stratospheric ozone depletion, or ecotoxicity, the use of a paper substrate causes only 10-20% of the environmental impact of PET.<sup>17</sup>

Bioplastics, such as cellulose derivatives PLA and cellulose acetate (CA), have been used to some extent as substrates for printed electronics.<sup>18</sup> Other potential candidates include bio-based PET, polycarbonate, and bio-based low-density polyethylene (LDPE).<sup>19</sup> Some bioplastics are biodegradable, such as PLA, polycaprolactone (PCL, **Cat Nos. 440744, 440752**), and polyglycolide (PGL).<sup>20</sup> Compared to plastic substrates, bio-plastic substrates have disadvantages concerning heat resistance and inherent brittleness. Still, these issues can be resolved by

increasing film crystallinity through orientation and annealing improvements. Bio-plastic substrates have been used for items such as Printed Circuit Boards (PCBs), hybrid integrated Light Emitting Diode (LED) foils, and smart labels.<sup>3,24,25</sup>

### Conductive Materials Beyond State-of-Art

Although substrates constitute bulk electronic circuit waste, the components, electrical leads, and soldering materials also contain scarce and/or environmentally harmful materials. While copper is traditionally used as the lead material in FR4-based PCBs, silver represents the state of the art in printed and flexible electronics due to excellent printing ink properties and general environmental stability, retaining these qualities even in particulate form and low-temperature processing. However, silver is well known as an anti-bacterial material and thus harmful to the natural environment, requiring recovery and recycling of the material, which are both cost and energy-intensive processing procedures.<sup>10</sup> Furthermore, silver is becoming a scarce resource and increasingly expensive to extract from natural sources. Consequently, various methods to reclaim silver are in development.<sup>21</sup>

Copper tracks in standard PCBs are made by etching, resulting in significant waste material that renders them unsuitable as ecological substrates. However, printable copper-based materials have been developed and are increasingly attractive as silver alternatives when careful steps are taken to reduce copper oxidation.<sup>22,23</sup> The sintering process is one of the key shortcomings of copper-based inks. However, converting resources completely to bulk copper can help the material achieve electrical conductivity analogous to printed silver. Because this process is conducted at low temperatures, it qualifies as an ecological substrate and flexible material. Current inks can be sintered at temperatures as low as 130–140 °C.<sup>24</sup>

It has been shown that the impact of switching from silver to copper (**Cat. No. 901889**) in printed antenna board manufacturing reduced the global warming potential by 28%. When implemented on a large scale, switching from silver to copper would bring significant reduction potential to printed electronics.<sup>19</sup> Mixing silver with more renewable materials such as graphene can also reduce silver usage.<sup>25</sup> **Table 2** illustrates that silver is unsustainable as a conductor material as the material supply is already threatened.<sup>26</sup> Copper supply is currently maintained, but the availability is limited from conventional sources. However, carbon in this context (not as carbon-based fuel) is abundant, and no supply issues are anticipated.

Carbon-based conductors are ideal from an environmental and ecological perspective, provided they demonstrate sufficient conductivity for the intended application. They can be produced and applied without using unsustainable chemicals, high energy processing, or water consumption. From a material property perspective, graphene (**Cat. No. 900561**), graphene nanoribbons (**Cat. Nos. 922714, 922676**), and carbon nanotubes (**Cat. Nos. 901019, 698849, 755125**) show superior electrical conductivity compared to metals including copper and silver (~10<sup>6</sup> S/cm). Still, in application, interfaces between high conductivity domains limit conductivity, resulting in a practical conductivity of 1–0.1 % of the metal conductivity.<sup>27</sup> Carbon conductivity can be increased with doping, adding processing steps and cost. However, doped graphene fibers can almost reach the level of Al/Cu/Ag wires.

**Table 2.** Availability of raw materials, achievable electrical conductivity, and price on the market. (\*conductivity referenced as a printed layer, \*\*carbon in the form of graphene-based printing ink)

| Conductive Material | Availability                                | Estimated market price | Conductivity    |
|---------------------|---|------------------------|-----------------|
| Silver              | Serious threat in the next 100 years        | 680 €/kg               | 0.005–0.01 Ω/□* |
| Copper              | Limited availability, future risk to supply | 6 €/kg                 | 0.01–0.05 Ω/□*  |
| Carbon              | Plentiful supply                            | 1–10 €/kg              | 1–10 Ω/□**      |

In general, printing ink production can be conducted using either solvent or water-based formulations. The desired application determines the suitability of water-based ink, as it usually is not compatible with hydro-phobic substrates, and the adhesion of water-based printed features is typically lower than that of solvents. Water-based ink generally requires higher drying temperatures and longer drying times, increasing environmental impact. That said, solvent-based inks emit toxic Volatile Organic Compounds (VOCs), and their effect on sustainability will depend entirely on the ability of the production facility to manage emissions.<sup>28</sup> When using printed silver nanoparticles, the contribution of conductors is typically the primary factor in environmental consequences, while the influence of other chemicals is much lower.<sup>6</sup>

Aluminum is a low-cost, abundant alternative to both copper and silver. While not directly environmentally hazardous, it is energy intensive to produce and recycle. Aluminum oxidizes very easily, but when applied in thick layers, its native surface oxide protects the lower levels from further oxidation. Therefore, aluminum is best applied in a thick layer as particle-based systems are impractical due to oxidation. Patterned layers of aluminum can be applied by foil transfer via various methods, the most common being thermal foil transfer.<sup>29</sup>

## Conclusion

Circular design enabling reusability and recyclability of electronics is critically important alongside waste stream management and material recovery. The work towards sustainable substrates is well underway and increasing effort is being directed towards more sustainable conductors. Optimistically, the first novel material recovery based on biodegradable substrates has been reported.<sup>30</sup> We anticipate these advances will be joined by renewable active components via bioelectronics in addition to the further exploitation of these materials' intrinsic properties.

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## Carbon Nanomaterials and Conductive Inks

### Conductive Carbon Nanotubes

| Name                          | Description   | Size                           | Cat. No.      |
|-------------------------------|---|--------------------------------|---------------|
| Carbon nanotube, multi-walled |  >95% carbon basis                   | 50-90 nm diameter              | <b>901019</b> |
|                               |  >98% carbon basis                   | O.D. × L 6-13 nm × 2.5-20 μm   | <b>698849</b> |
|                               |  >8% carboxylic acid functionalized | avg. diam. × L 9.5 nm × 1.5 μm | <b>755125</b> |
| Graphene                      | electrical conductivity >103 S/m  | avg. no. of layers < 3         | <b>900561</b> |
| Graphene nanoribbon           | ≥90% carbon basis (EA)  | 0.25-0.35 μm                   | <b>922714</b> |
|                               | oxidatively splitted from CNT   | width: ≥200 nm nanoribbon      | <b>922676</b> |

### Conductive Carbon Nanotubes

| Name  | Description  | Resistance  | Cat. No.      |
|---|--|---|---------------|
| Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) |  0.8% in H <sub>2</sub> O, conductive inkjet ink  | 110 Ω/sq  | <b>739316</b> |
| Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) |  5.0 wt. %, conductive screen printable ink   | ≤130 Ω/sq   | <b>768650</b> |
| Graphene ink  |  for inkjet printing, with ethyl cellulose in cyclohexanone and terpineol, inkjet printable | 0.003-0.008 Ω-cm (thermally annealed 250°C for 30 minutes, film thickness >100 nm)  | <b>793663</b> |
| Graphene ink in water                                   |  screen printable   | 10 Ω/sq, at 25 μm thickness   | <b>808261</b> |
| Graphene ink in water                                   |  inkjet printable   | 4k Ω/sq, 80 nm thickness  | <b>808288</b> |
| Graphene/PEDOT:PSS hybrid ink                           | dispersion in DMF  | 500 Ω/sq, 20 nm film: 80% transmittance   | <b>900442</b> |
| Graphene dispersion                                     |  ≥0.2 mg/mL in DMF, sheet resistance 2 kΩ/sq  |   | <b>900448</b> |
| Graphene dispersion                                     |  1 mg/mL in DMF, sheet resistance 4.8 kΩ/sq   |   | <b>900450</b> |
| Graphene ink  |  for inkjet printing, photonic annealable   | 0.003-0.008 Ω-cm, thermally annealed 300 °C for 30 minutes, film thickness >100 nm  | <b>900695</b> |
| Graphene ink for spin/spray coating photonic annealable |  for spin-coating, spray-coating, photonic annealing  | 0.003-0.005 Ω-cm, sample prepared by spin-coating at 2000 rpm/30 s for 5 coats, followed by thermal annealing at 300 °C in air for 30 minutes | <b>900960</b> |

## Flexible Substrates

### Biodegradable Materials for Substrates

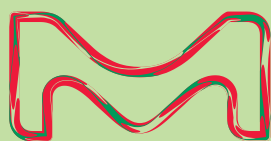
| Name                            | Description   | Viscosity                          | Form                   | Cat. No. |
|---------------------------------|---|------------------------------------|------------------------|----------|
| Bio-based polyether polyol      | $M_n$ 400-600 Da  | 90-120 mPa.s(40 °C)                |                        | 923990   |
|                                 | $M_n$ 2600-2800 Da  | 1550-1850 mPa.s(40 °C)             |                        | 923982   |
|                                 | $M_n$ 1800-2200 Da  | 750-900 mPa.s(40 °C)               | solid                  | 923966   |
| Poly(D,L-lactide)               | average $M_n$ 5,000, PDI $\leq$ 1.1                               |                                    | solid                  | 764612   |
|                                 | average $M_n$ 10,000, PDI $\leq$ 1.2                              |                                    | solid                  | 764620   |
|                                 | average $M_n$ 10,000, PDI $\leq$ 1.2                              | 200-300 mPa.s(40 °C)               | solid                  | 923974   |
|                                 | average $M_n$ 20,000 (NMR), PDI $\leq$ 1.3                        |                                    | crystals               | 767344   |
| Poly(L-lactide-co-caprolactone) | lactide:caprolactone 60:40  | viscosity 1.5 dL/g                 | chips or granules      | 900300   |
|                                 | lactide:caprolactone 35:65  | viscosity 1.5 dL/g                 | chips or granules      | 900321   |
|                                 | lactide:caprolactone 15:85  | viscosity 1.5 dL/g                 | chips or granules      | 900312   |
| Poly(L-lactide-co-glycolide)    | L-lactide:glycolide 5:95  | viscosity $\geq$ 1.1 dL/g          | granular               | 790214   |
|                                 | lactide:glycolide 65:35   | viscosity 0.6 dL/g                 | granular               | 900316   |
|                                 | lactide:glycolide 20:80   | viscosity 1.6 dL/g                 | chips or granules      | 900289   |
|                                 | lactide:glycolide 10:90   | viscosity 1.7 dL/g                 | chips                  | 901021   |
| Polycaprolactone                | average $M_w$ $\sim$ 14,000<br>average $M_n$ $\sim$ 10,000 by GPC | 400-1000 mPa.s, 50 wt. % in xylene | flakes or chunk(s)     | 440752   |
|                                 | average $M_n$ 80,000  |                                    | pellets ( $\sim$ 3 mm) | 440744   |

### Recyclable Flexible Substrates

| Name                             | Thickness       | Dimensions                 | Cat. No.   |            |
|----------------------------------|-----------------|----------------------------|------------|------------|
| Polyethylene Terephthalate, film | 0.013 mm        | 100 × 100 mm               | GF98750021 |            |
|                                  |                 | 150 × 150 mm               | GF25034868 |            |
|                                  |                 | 300 × 300 mm               | GF73361639 |            |
|                                  |                 | 600 × 600 mm               | GF89357619 |            |
|                                  | 0.038 mm        | 150 × 150 mm               | GF68553793 |            |
|                                  |                 | 300 × 300 mm               | GF63493476 |            |
|                                  |                 | 610 × 610 mm               | GF02023243 |            |
|                                  |                 | L 1 m                      | GF43135871 |            |
|                                  | 0.05 mm         | 150 × 150 mm               | GF34652707 |            |
|                                  |                 | 300 × 300 mm               | GF31588229 |            |
|                                  |                 | 600 × 600 mm               | GF48528591 |            |
|                                  |                 | L 0.2 m, coil width 315 mm | GF67321469 |            |
|                                  |                 | L 0.5 m                    | GF02673581 |            |
|                                  | 0.075 mm        | 125 × 125 mm               | GF94440573 |            |
|                                  |                 | 150 × 150 mm               | GF08830548 |            |
|                                  |                 | 254 × 254 mm               | GF05263635 |            |
|                                  |                 | 300 × 300 mm               | GF03818280 |            |
|                                  |                 | 600 × 600 mm               | GF77285627 |            |
|                                  |                 | L 1 m                      | GF35936365 |            |
|                                  |                 | L 1 m                      | GF60703286 |            |
|                                  | 0.1 mm          | 100 × 100 mm               | GF69672000 |            |
|                                  |                 | 150 × 150 mm               | GF99278713 |            |
|                                  |                 | 300 × 300 mm               | GF09063581 |            |
|                                  |                 | L 0.5 m                    | GF92639986 |            |
|                                  | 0.125 mm        | 300 × 300 mm               | GF32099272 |            |
|                                  |                 | 600 × 600 mm               | GF15459756 |            |
|                                  |                 | L 1 m                      | GF51233048 |            |
|                                  | 0.175 mm        | 150 × 150 mm               | GF35954826 |            |
|                                  |                 | 300 × 300 mm               | GF94353598 |            |
|                                  |                 | 600 × 600 mm               | GF52295621 |            |
|                                  |                 | L 0.5 m                    | GF45117075 |            |
|                                  |                 | L 0.5 m                    | GF51809799 |            |
|                                  | 0.25 mm         | 300 × 300 mm               | GF25214475 |            |
|                                  |                 | L 0.5 m                    | GF51809799 |            |
|                                  | Polyimide, film | 0.025 mm                   | L 5 m      | GF77686521 |

## Flexible Substrates Coated with Conductive Material

| Name   | Dimensions  | Resistance | Cat. No. |
|--|---|------------|----------|
| Indium tin oxide coated PEN                                      | 29.7 cm × 21 cm × 125 μm  | <15 Ω/sq   | 917826   |
|  | 9.6 cm × 9.6 cm × 125 μm  | 5 Ω/sq     | 917311   |
| Indium tin oxide coated PEN with titanium(IV) oxide buffer layer | 29.7 cm × 21 cm × 125 μm  | <15 Ω/sq   | 918067   |
| Indium tin oxide coated PET                                      | 1 ft × 1 ft × 5 mil   | 60 Ω/sq    | 639303   |
|  | 1 ft × 1 ft × 7 mil   | 60 Ω/sq    | 749729   |
| Monolayer graphene film  | 1 in. × 1 in. × (theoretical) 0.345 nm, monolayer graphene film | 700 Ω/sq   | 745863   |
|  | 1 in. × 1 in. × 0.188 mm, PET film substrate                    |            |          |
|  | 2 in. × 2 in. × (theoretical) 0.345 nm, monolayer graphene film | 700 Ω/sq   | 745871   |
|  | 2 in. × 2 in. × 0.188 mm, PET film substrate                    |            |          |



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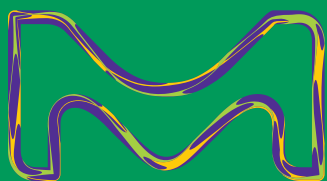


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